PAN NORTH AMERICA
Pesticide Action Network

# Pesticide Drift Monitoring in Minnesota

## JUNE 13, 2006 - AUGUST 13, 2009

## Technical Report

PESTICIDE ACTION NETWORK NORTH AMERICA

MAY 2012

## Pesticide Action Network North America
## May 17, 2012

Pesticide Action Network North America (PAN North America) works to replace the use of hazardous pesticides with ecologically sound and socially just alternatives.

As one of five PAN Regional Centers worldwide, we link local and international consumer, labor, health, environment and agriculture groups into an international citizens' action network. This network challenges the global proliferation of pesticides, defends basic rights to health and environmental quality, and works to ensure the transition to a just and viable society.

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## List of Abbreviations

| | |
|---|---|
| ARB | Air Resources Board, the California agency in charge of regulating air pollution in the state. |
| ATSDR | Agency for Toxic Substances and Disease Registry, the agency within the U.S. Department of Health and Human Services that "performs specific functions concerning the effect on public health of hazardous substances in the environment." |
| DPR | California Department of Pesticide Regulation, the California agency in charge of regulating pesticides in the state. |
| HEC | Human Equivalent Concentration. An endpoint (NOAEL or LOAEL) air concentration determined from animal studies that has been adjusted to account for differences in uptake of the chemical through the lungs between animals and humans. |
| FQPA | The Federal Food Quality Protection Act. Passed in 1996, this law substantially revised the way U.S. EPA evaluates pesticides for registration, requiring them to account for the special vulnerability of children and women of child-bearing age. |
| $LD_{50}$ | A dose that is lethal to 50% of test animals of a given species. Commonly expressed in units of mg/kg, $LD_{50}$ values are used to rank the acute toxicity of chemicals. |
| LOQ | Limit of Quantitation, the lowest concentration at which a laboratory can reliably measure the amounts of a pesticide present in a sample. See **Calculations** section for details. |
| MDL | Method Detection Limit, the lowest concentration that can reliably be detected for a sample collected and analyzed according to a specific method. See **Calculations** section for details. |
| NIOSH | National Institute for Occupational Safety and Health, the federal agency that oversees worker safety. |
| NOAEL | No Observable Adverse Effect Level, the toxicological dose of a chemical below which no adverse effects are anticipated from exposure to that chemical alone, usually in units of mg/kg-day. |
| OP | Organophosphorus compound, usually insecticides. Most OPs are neurotoxic, inhibiting the activity of cholinesterase, an enzyme necessary for the proper functioning of the nervous system. |
| REL | Reference Exposure Level, the concentration of a chemical in air, derived from the U.S. EPA-selected NOAEL, below which no adverse effects are anticipated from exposure to that chemical alone, given in units of $ng/m^3$. See **Calculations** section for details. A REL represents a level of concern for inhalation exposure analogous to the Reference Dose U.S. EPA uses to assess levels of concern for dietary exposure. |
| SOP | Standard Operating Procedure, a written method for conducting sampling, analysis and other laboratory protocols. See Appendix 3 for an example. |
| U.S. EPA | United States Environmental Protection Agency, the federal agency charged with regulating pesticides, air, water, hazardous waste sites, and more. |
| USDA-ARS | United States Department of Agriculture-Agricultural Research Service, the research arm of the USDA. One part of their work is to evaluate the fate and transport of pesticides in the environment. |
| USGS | United States Geological Survey, a federal agency that, among other activities, evaluates airborne pesticides as a source of water pollution. |

## Executive Summary

This report presents the results of monitoring for airborne pesticides conducted between June 2006 and August 2009 in central Minnesota. Overall, the results of the study indicate that for several months each summer, central Minnesota residents in potato-growing areas are regularly exposed to low to moderate levels of the commonly used fungicide chlorothalonil in air.

Drift Catcher sampling devices were stationed in 19 locations in the communities of Browerville, Frazee, Perham, Pine Point, Staples and Waubun. Usually samplers were placed on porches, in windows, or in yard areas where children often played. In some locations where effects on livestock or crops were the primary concern, the samplers were located near barns and animal pens instead of near homes. Fifteen of the locations were near agricultural land, and four in residential areas. One of the samplers was stationed near a school.

A total of 340 field samples were taken. Residues of one or more pesticides were detected in 224 (66%) of the samples, and pesticides were detected in samples from all but two sites. Chlorothalonil—used mainly on potatoes in Minnesota—was found in 64% of samples that were tested for it.

The maximum concentration of chlorothalonil found in any sample (317 ng/m$^3$) was collected near the community of Frazee, July 25–26, 2008. Time-weighted average chlorothalonil concentrations at the various sites ranged from 0 to 56 ng/m$^3$, with the highest time-weighted average concentration of 56 ng/m$^3$ observed near Staples, MN from June 27–July 12, 2006.

The ambient chlorothalonil concentrations documented in this study were compared with those measured by the California Air Resources Board near an application site. The highest levels observed near the residential and school sampling sites in Minnesota are approximately 43% of the peak concentration observed within 60-100 feet of an application (740 ng/m$^3$), and are comparable to concentrations measured in an ambient air monitoring study in Canada and in another Drift Catcher monitoring project in Florida.

### Chlorothalonil health standards shifting

The significance of exposure to the levels of chlorothalonil in the air measured in this study is unclear as the "Level of Concern" established by regulatory agencies has changed several times in recent years, and EPA is currently reevaluating the toxicity of chlorothalonil based on exposures through inhalation rather than ingestion.

The Reference Exposure Level (REL) for a one-year-old child calculated from EPA's Level of Concern has changed several times since 1999. In the 1999 Reregistration Evaluation Decision document, the REL was 34,000 ng/m$^3$. In a 2007 tolerance decision, it was 52,000 ng/m$^3$; in a 2008 tolerance decision, it was 51,000 ng/m$^3$, based on a different toxicological study than the 2008 value. Similarly, the California Department of Pesticide Regulation (DPR) developed a Screening Level of 560 ng/m$^3$ based on an inhalation toxicity study in 2003, but changed it to 34,000 ng/m$^3$ based on an oral toxicity study in 2007.

In the March 28, 2012 Scoping Document for the Registration Review of chlorothalonil, EPA proposed to use an acute inhalation study as the basis for their Level of Concern, which gives an inhalation-based REL of 260 ng/m$^3$, but this value has not been finalized as of May 2012. The development of a proper evaluation of the inhalation toxicity of chlorothalonil should be a high

priority for both EPA and the California Department of Pesticide Regulation and should include evaluation of a valid inhalation toxicity study designed to capture NOAELs at low doses.

Chlorothalonil is ranked as a "B2, probable" carcinogen by EPA. Lifetime cancer risks based on the measured chlorothalonil exposure at the sampling sites were all less than one additional cancer per million people (the generally accepted standard for acceptable cancer risk), at 0.014 per million, assuming the oral study on which the cancer potency is based is a valid measure for inhalation exposure.

## Mixture of pesticides

The Drift Catcher results also document that rural communities in central Minnesota are exposed to mixtures of pesticides in air.

The fungicide pentachloronitrobenzene (PCNB, also known as quintozene) was found in 57% of the 14 samples taken at a Browerville site in 2006, and the herbicide 2,4-D ethylhexyl ester was found at two Frazee sites and one Perham site in 2008, with a detection rate of 72% of the 29 samples tested during the sampling period. Chlorpyrifos, a neurotoxic organophosphate insecticide, was found near Browerville in 2006 and Perham in 2009, with 33% of the 40 field samples containing measureable levels.

A total of 42 samples (12%) were found to contain more than one pesticide, with seven samples (2.4%) containing a combination of chlorothalonil, PCNB and chlorpyrifos. Ten samples (3%) from two sites at Pine Point contained a mix of chlorothalonil and pendimethalin.

Sampling near hybrid poplar plantations resulted in no detections above the method detection limit for the low-volatility pesticides associated with this crop—clopyralid and quizalop-P-ethyl. Additionally, no samples were found to contain the ethylene bis(dithiocarbamate) (EBDC) fungicides maneb and mancozeb, fungicides also used on potatoes. These fungicides are not especially volatile after application. We did not sample for ethylene thiourea (ETU), a volatile and toxic breakdown product of the EBDC fungicides.

# Introduction

In 2006, an organized group of citizens and family farmers in central Minnesota contacted Pesticide Action Network (PAN) and requested assistance in determining whether they were being exposed to drifting pesticides. In previous years, each had suffered deteriorations in health and/or unexplained losses of crops, livestock, or bees. These events coincided with the establishment of new industrial agricultural operations adjacent to their homes and farms. These new operations, typically run by or under contract with large agricultural companies, applied pesticides frequently. These concerned individuals suspected that chemicals drifting out of these fields might have something to do with their problems.

Similarly, in 2007 the White Earth Land Recovery Project, a non-profit organization on the White Earth Reservation in central Minnesota, requested PAN's assistance in determining whether the Pine Point community was impacted by adjacent agricultural operation. Of particular concern was the tribal elementary school, located directly across the road from a large field frequently sprayed with pesticides.

The initial goal of this sampling project was to identify any pesticides drifting out of fields and into people's yards and to determine which crop or crops were linked most directly to the pesticide drift. Upon analyzing the first year's samples, it became apparent that chlorothalonil was frequently in the air near potato fields. Therefore, subsequent sampling focused on sites near potato fields.

## Site Selection

Initial sampling sites for this study were selected on the basis of participants' concerns about pesticide exposure. They identified two crops of particular interest: potatoes and hybrid poplar.

As discussed in detail later in this report, sampling in 2006 resulted in no detections above the method detection limit of pesticides associated with hybrid poplar production—clopyralid and quizalop-P-ethyl. In contrast, chlorothalonil—a fungicide commonly used on potatoes in Minnesota—was frequently found in samples collected near potato fields, and not detected in samples from a site located far from potatoes, but close to wheat, corn, and soybeans. Therefore, subsequent sampling in 2007–2009 focused on areas near potato-growing operations.

In all cases, sampling devices were stationed outside at private homes, farms, and at one site, a school. Usually samplers were placed on porches, in windows, or in yard areas where children often played. **Figure 1** shows a typical sampling site. In some locations (Frazee), where effects on livestock or crops rather than on human health were the primary concern, the samplers were located near barns and animal pens instead of near houses.

**Figure 1:** A Drift Cather sampling device (on patio) collecting a sample at a typical site in 2008.

## Minnesota potato production

As shown in **Table 1**, about 50,000 acres of potatoes are planted in Minnesota every year, valued at $130–170 million, annually. Minnesota ranks sixth in potato production in the country; however, within the state comparatively little farmland is devoted to the crop. In 2008, more than seven million acres each of corn and soybeans were planted, along with almost two million acres of wheat. More acres were also devoted to oats, barley, sugar beets, sunflower, edible beans and green peas than to potatoes that year.[1]

**Table 1: Acres of Potatoes Planted and Harvested in Minnesota, 2006–2009**

| Year | Acres Planted | Acres Harvested |
|---|---|---|
| **2006** | 53,000 | 50,000 |
| **2007** | 52,000 | 49,000 |
| **2008** | 50,000 | 48,000 |
| **2009** | 47,000 | 45,000 |

*Source:* Reference 1.

According to University of Minnesota Extension, the principal areas of potato production in the state are the northern Red River Valley, areas with sandy soils from Elk River to Park Rapids, and a small area along the southern border of the state near Albert Lea.[2] County level data on potato production is not available, but the U.S. Department of Agriculture (USDA) does provide

information for multi-county Agricultural Statistics Districts. In 2007, more potatoes were planted in the Central district than any other, and this district also had the highest density of production (i.e. potato acreage divided by total acreage for the district).[1] (See **Figure 2)**.

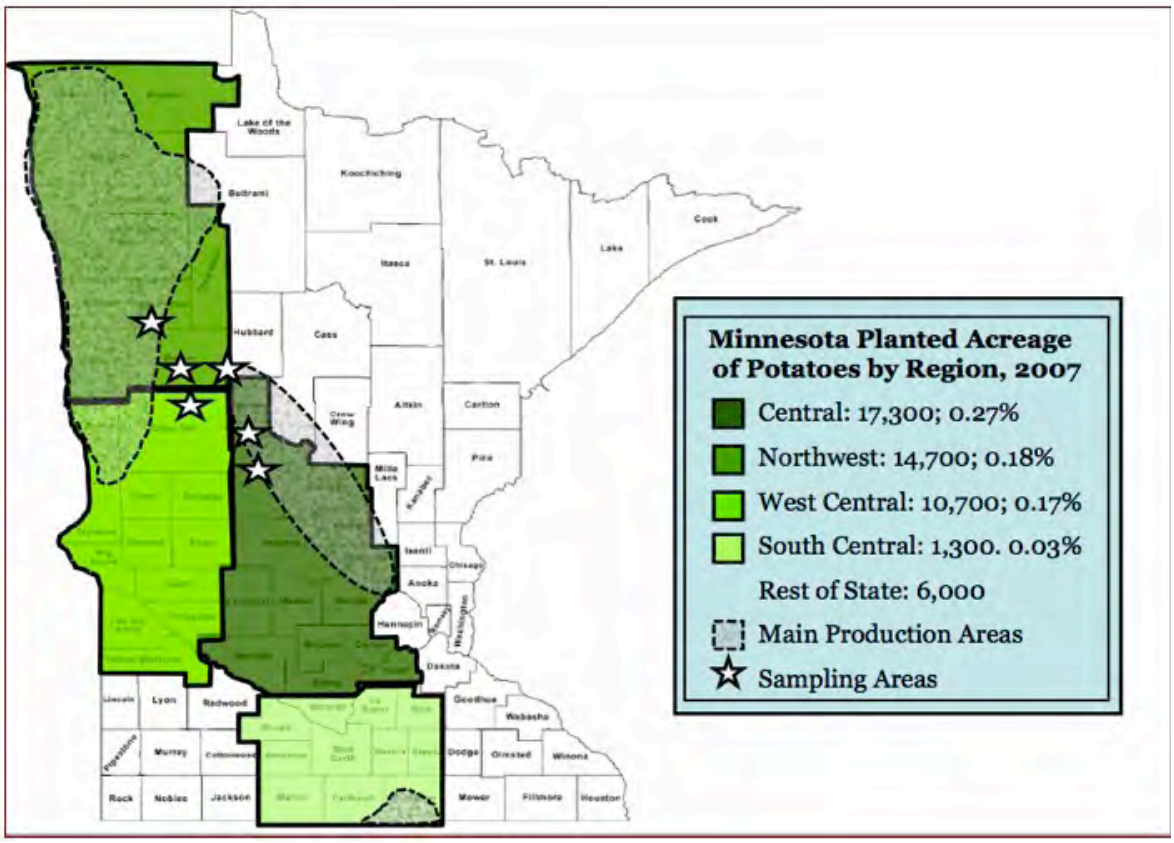



**Figure 2:** The density of Minnesota potato production, derived from USDA NASS data (Reference 1), is shown in green. Main production areas are shown in speckled green-gray, adopted from the University of Minnesota Extension's potato factsheet in Reference 2.

## Pesticide use on potatoes

According the National Agricultural Statistics Service, in 2005 (the most recent year for which data for potatoes was reported) fungicides were applied to 98% of Minnesota potato acres. The most common was chlorothalonil, which was applied to 83% of acres. On average, 9.9 applications of chlorothalonil were made to each field annually. In total, 399,000 lbs of chlorothalonil were applied in the state that year.[3]

Mancozeb is another commonly used fungicide in the state, applied to 75% of potato acres in 2005. On average 3.3 applications of mancozeb were made to fields that year, amounting to a statewide total of 152,000 lbs.[3] Fungicides are often applied by chemigation using the center pivot irrigation systems used for watering the potatoes (see **Figure 3**).

Herbicides and insecticides are also common in Minnesota potato production, with 97% of acres receiving applications in 2005. Use of these pesticides is much less intense than fungicides, with only 33,000 lbs of herbicides and 10,000 lbs of insecticides used in 2005.[3]

Project participants report that the potato fields near their homes are spayed on a weekly basis during the summer.

**Figure 3:** Application of pesticides to potatoes is frequently conducted by chemigation using center-pivot irrigation rigs.

## Individual Sampling Sites

To preserve the anonymity of project participants, physical addresses of the sampling sites are not disclosed. The towns near the sampling sites are shown in **Figure 2**. Six individual sampling areas were used.

### Browerville

Browerville is in Todd County, which is part of Minnesota's Central Agricultural Statistics District, the district with the most intensive potato production in 2007 (**Figure 2**) and 2006 (data not shown, calculated from Reference 4). Samples were collected from five sites in the Browerville area in 2006–2007. All sites were rural homes bordering farmland. **Figure 4** depicts Browerville Site A, which is typical of the Browerville sites. According to the information submitted by the project participant, the two center pivot fields directly to the east of the sampling site (approximately 35 acres, each) were planted in potatoes in 2006, as indicated in **Figure 4.** The sampling device was approximately 150 feet from the edge of the nearest field.

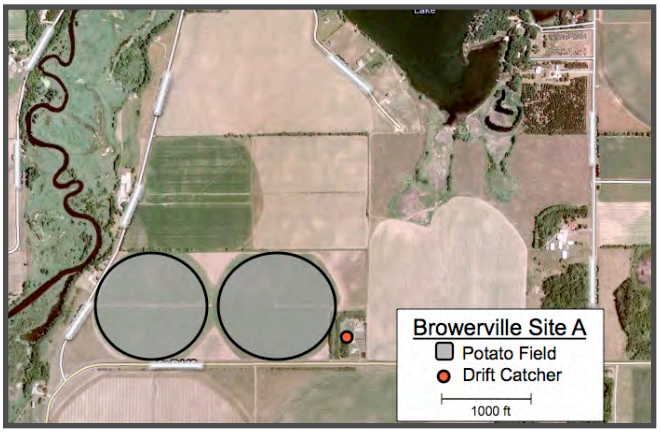



**Figure 4:** Browerville Site A.

Browerville Site B was a home next to a soybean field and approximately 0.3 miles north of the nearest potato field. Site C was located approximately 0.2 miles west of two 160-acre pivots that were planted in potatoes in 2006, according to the person collecting the samples.

Hybrid poplar trees were the primary concern at Browerville Sites D and E. Site D was about 0.1 mile northeast of about 100 acres of hybrid poplar and about 0.6 miles southwest of another 200 acres. Site E was located approximately 0.1 miles north of 80 acres of hybrid poplar. The 20-acre field in between this sampling site and the hybrid poplar was planted in corn in 2006. The project participant did not indicate the presence or absence of potato fields near these sites.

## Frazee

Frazee is located on the border of Becker and Otter Tail Counties. Becker County is in Minnesota's Northwestern Agricultural Statistics District, the district with the second most intensive potato production in 2007. Otter Tail County is the West Central district, ranked third. Samples were collected from six sites in Frazee between 2006 and 2008. As with the Browerville sites, all sites were rural homes bordering farmland; no samples were collected from Frazee's downtown area. All were located in the same general area as depicted in **Figure 5**.

In 2006, sampling took place only at Frazee Site A. The operator indicated that about 0.4 miles to the south of this site there was a field planted in potatoes that year that was one-mile long by half mile wide.

In 2007, samples were collected at Frazee Sites A, B, C and F. In 2008, sampling took place at Sites D and E. **Figure 5** indicates the fields in the immediate vicinity that were planted in potatoes each year. **Figures 6** and **7** show the landscape surrounding Frazee Sites C and F.

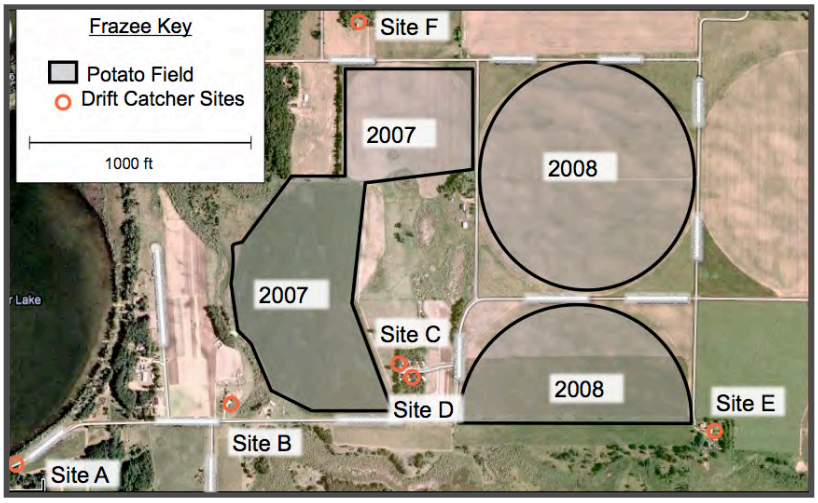



**Figure 5:** Frazee Sites A–D and F. Dates indicate years when fields were planted in potatoes.

**Figure 6:** A helicopter sprays pesticides on a potato field adjacent to Frazee Site C in 2007. The mobile home next to the field was unoccupied when this picture was taken.

**Figure 7:** A spray helicopter maneuvers near Frazee Site F in 2008.

## Perham

Perham is south of Frazee and entirely within Otter Tail County, which is a part of Minnesota's West Central Agricultural Statistics District—the district with the third most intensive potato production in 2007. Perham Sites A and B were homes located in rural agricultural areas. Sampling at these sites took place in 2008. Perham Site A was located about one mile away from the closest potato field, which was about 50 acres in size. Perham Site B was located about two miles north of Site A, about 0.2 miles south of a 100-acre potato field, and 0.3 miles west of 70 acres more of potatoes. According to the person collecting the samples, "The samples at [Perham Site A] were quite protected by trees and [the sampler] could not be out in the open because of kids coming to stay."

In contrast to the all the other sites in this study, Perham Site C was located in a dense suburban area rather than a rural area. Specifically, the sampling site was in the southwest section of the city, near Perham Memorial Hospital and within a few hundred feet of Heart of the Lake Elementary School. The closest potato field (80 acres) was almost a half-mile to the west. Samples were collected here in 2009 only.

## Pine Point

Samples were collected from a school and a residential site near Pine Point in 2007. Pine Point is in Becker County. It is also on the White Earth Indian Reservation. At Site A, the Drift Catcher was sited on the roof of a school building, by the HVAC air intake, at a distance of 221 feet from an agricultural field. In 2007, this agricultural field, which is immediately adjacent to Site A, was planted with dry edible beans. Site A was located next door to a church and community center. Site B was located at a private residence, 144 feet away from the nearest potato field. Site B was surrounded on two sides by potato fields.

## Staples

Staples straddles Wadena and Todd Counties, both of which are in Minnesota's Central Agricultural Statistics District, the district with the most intensive potato production in 2006. Samples were collected from two sites in Staples in 2006, both in Wadena County. Both sites were homes surrounded by agriculture, but the Drift Catcher operator at these sites did not record any information about the types of crops growing in the immediate vicinity.

## Waubun

Samples were collected from a residential site near Waubun in 2006. Waubun is in Mahnomen County, which is part of the Northwestern Agricultural Statistics District, the district with the second most intensive potato production in 2006. It is also on the White Earth Indian Reservation. The fields immediately surrounding the sampling site were planted in corn, wheat and soybeans. No potatoes were planted in the immediate area of the sampling site, and the person collecting the samples believed the nearest potato field was probably at least 20 miles away.

# Methods

## Sample collection

The Drift Catcher™ air monitoring device was designed based on sampling equipment used by the California Air Resources Board. This design has been evaluated by a Scientific Advisory Committee comprised of scientists from the California Department of Pesticide Regulation, the California Air Resources Board, U.S. EPA Region 9, the U.S. Geological Survey and the California Department of Health Services.

Between 2006 and 2009, a total of 340 field samples and 43 trip blank samples were collected using Drift Catcher devices across 19 sites within six sampling areas in central Minnesota. (See Site Description section for details of where samplers were stationed.) Samples were collected by passing a measured volume of air through XAD-2 resin tubes obtained from SKC Inc. (75/150 mg, Cat. #226-30-05). Sample tubes were normally changed once per day during the sampling periods in approximately twenty-four hour intervals, although a few samples were collected over multiple days. Consult the "Total Sample Time" column in the tables in **Appendix 1** for information on individual sample times. This sampling method was based on NIOSH method 5600 for organophosphorus insecticides[5] and the CA Air Resources Board sampling protocols used in the Toxic Air Contaminant monitoring program.[6]

The air sampling device consists of a vacuum pump (McMaster Carr #41675K41) connected with 3/8" Teflon tubing and compression fittings to a manifold equipped with two Cajon-type, vacuum-tight Teflon fittings (Beco Mfg.) as tube holders. Flow controller valves for each sample allowed for adjustment of air flow to each tube independently (**Figure 8**).

Pre-labeled sample tubes were attached to the manifold, which stood approximately 1.5 meters off the ground. Flow rates were measured with a 0–5 L capacity rotameter (SKC Inc., Cat. #320-4A5) pre-calibrated with a mass flow meter (Aalborg, cat. #GFM17A-VADL2-A0A). The flow rate was set at the beginning of the sampling run to 2.0 liters per minute and measured again at the end of the sampling period. If the difference between the start and stop flow rates was less than 25%, the average of two values was used to calculate the sample volume. If the ending flow rate differed by more than 25% from the starting flow rate, the greater flow rate was used, giving a conservative (lower) value for the final pesticide concentration.

Sample tubes were covered with mylar light shields during the sampling period to prevent any photolytic degradation of the sample. Sample identification, start and stop times, and flow rates were recorded on the Sample Log Sheet (**Appendix 5**). In addition, wind speed and direction, temperature, weather conditions, and any additional observations were noted at the beginning and end of each sampling period. At the end of each sampling period, labeled tubes were capped and placed in a zip-lock plastic bag with the completed log sheet.

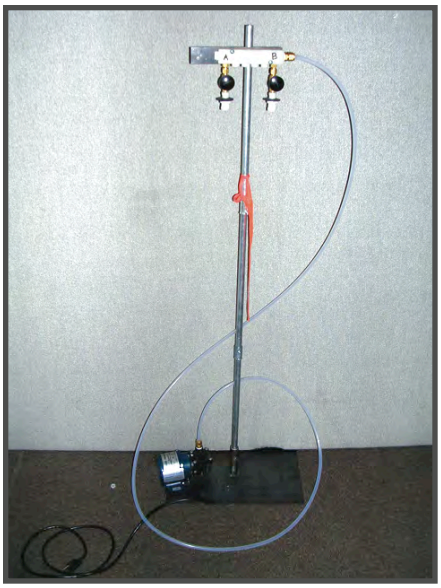
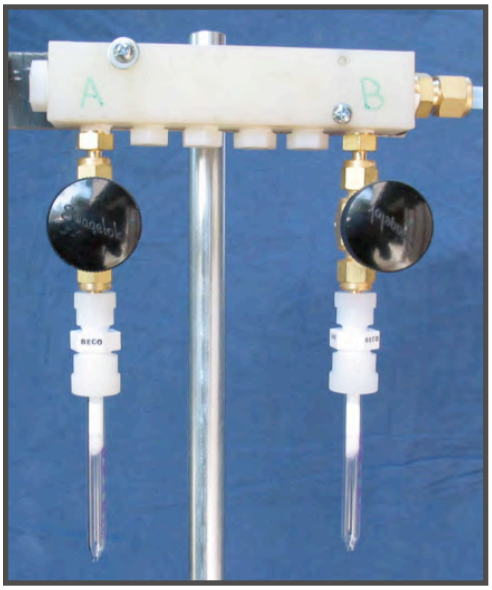
(a)  (b) 


**Figure 8:** (a) The Drift Catcher™ air monitoring device. (b) Drift Catcher manifold with flow control valves.

Within 10 minutes of removal from the sampling manifold, samples were placed into a -10°C freezer. After storage for no more than three months, samples were shipped to the PAN laboratory (University of California, Berkeley) at -10 to 0°C by overnight express mail for analysis. A chain of custody form (**Appendix 6)** accompanied each batch of samples during handling and transport.

In the laboratory, samples were entered into the sample log database (**see Appendix 8**) and stored in a -20°C freezer prior to processing and analysis, which occurred within four months of receipt in the laboratory. Alternatively, some of the samples were shipped to a commercial lab for analysis that was conducted within three weeks of sample receipt. Prior sample storage stability assessments conducted by the California ARB indicate no decomposition of analytes held at -20°C on XAD-2 resin for as long as 24 days for chlorothalonil[7] and 37 days for chlorpyrifos.[8] Stability data for clopyralid, quizalofop-ethyl, and PCNB were not available; however, all of these compounds have long soil half-lives at ambient temperatures[9] and are unlikely to degrade appreciably in a -20°C freezer.

## Sample analysis

A total of 322 samples were analyzed for chlorothalonil. Of these, 200 were analyzed in PAN's laboratory using a multi-residue method capable of detecting chlorothalonil, and 122 were analyzed by a commercial lab. Of the samples analyzed by the commercial lab, 109 were analyzed exclusively for chlorothalonil and 13 (those from Staples Site A) were analyzed using a multi-residue screen.

### PAN analysis

Detailed standard operating procedures for processing sorbent tubes were developed from NIOSH method 5600[5] and the methods used by CA ARB[7] and are attached as **Appendix 7**. Briefly, the front and rear XAD-2 resin beds were each extracted with 2.00 mL of pesticide-grade ethyl acetate using sonication, and the extracts were analyzed using a Varian 3800 gas chromatograph equipped with an 8400 autosampler using split injection. Samples were quantified using an electron capture detector (ECD). Confirmation of peak identity was done using mass spectrometry. The details of instrumental conditions can be found in **Appendix 9.**

The analytical method employed for identifying pesticides was a multi-residue screen, used in previous PAN investigations[10] to identify in field samples the organophosphates chlorpyrifos, malathion, azinphos-methyl, and naled; the organochlorines DDE and chlordane; the pyrethroid permethrin; the herbicides molinate and pendimethalin. The screen is also sensitive to a variety of other organophosphates, pyrethroids, and thiocarbamates, as indicated by injections of their stock solutions giving excellent responses on our instrument. This method is not sensitive to most carbamate insecticides, chlorophenoxy herbicides, metal-based compounds, or other herbicides. Trip blanks were analyzed with the same batch of field samples that they were shipped with, using identical methods.

Concentrated standards of chlorothalonil, chlorpyrifos, PCNB, clopyralid, quizalofop, and 2,4-D ethylhexyl ester for use in analysis were obtained directly from Accustandard (Catalog numbers P-222S, P-094S, P-113S, P-488S, P-293S-CN, P-439S-H respectively), at concentrations of 100 µg/mL in methanol, acetonitrile, or hexane. Five to seven dilute analytical standards were prepared from the stock solution using pesticide-grade ethyl acetate as diluent. Standards spanned the anticipated concentration range for the samples in the linear response range for the detector. Samples that were initially determined to contain the analyte in amounts less than the Limit of Quantitation (LOQ) for the initial method were reanalyzed using a more sensitive method with a lower LOQ. Sensitivity was enhanced by adjusting the injector split ratio. Samples that were above the range of the calibration curve were diluted and reanalyzed. Samples with pesticide concentrations above the method detection limit (MDL) but below the limit of quantitation (LOQ) were estimated at half of the LOQ. The calculation of pesticide air levels from gas chromatograph results is described in the **Calculations** section.

### Commercial lab analysis

Some of the samples for this project were sent to Environmental Micro Analysis, Inc. (Woodland, CA; ELAP Certificate #2211) for analysis and analyzed by EMA Labs' CDFA multi-residue screen, capable of detecting over 100 common insecticides, fungicides and herbicides. Those analyzed for chlorothalonil only were examined using EMA's organochlorine screen, and clopyralid and quizalofop were analyzed using NIOSH method 5602. EBDC fungicides were analyzed by EMA's EBDC screen, which involves transforming any EBDC residues into $CS_2$ which is then quantified. Detection limits for these methods are noted in the Results section below. In addition to the field samples, trip blank samples and spiked samples were also sent to the lab for analysis. The lab was unaware of which samples were field samples and which were blanks or spikes. No pesticides were detected in any of the blanks.

Spiked samples were evaluated by EMA labs to assess recoveries. Three samples spiked with chlorothalonil were analyzed; their fortification levels and recoveries were: 3.0 µg/tube, 73%; 3.0 µg/tube, 48%; and 1 µg/tube, 79%. For clopyralid, recoveries of 61% and 50% were obtained for tubes fortified with 1 µg and 3 µg clopyralid, respectively. For quizalofop,

recoveries were 179% and 162% for tubes fortified with 1 µg and 3 µg quizalofop, respectively. Results from the commercial lab were not corrected for these percent recoveries. No EBDC-spikes were sent to the lab.

## Results

Residues of one or more pesticide were detected in 224 (66%) of the field samples, and pesticides were detected in field samples from all but two sites. The fungicide chlorothalonil was by far the most commonly detected pesticide. Also detected were chlorpyrifos, an organophosphate insecticide; the fungicide pentachloronitrobenzene ("PCNB", also known as quintozene); and the herbicide 2,4-dichlorophenoxyacetic acid ethylhexyl ester ("2,4-D"). Selected samples thought to contain quizalofop-p-ethyl, clopyralid, and/or ethylenebisdithiocarbamate (EBDC) fungicides (maneb, mancozeb, ziram) were examined for these specific analytes, but none was found. A sampling timeline is provided in **Figure 9**. Chlorothalonil results for each site are summarized in **Table 2**; see **Appendix 1** for complete data for each site. The results for the other pesticides are included in the tables in Appendix 1.

No pesticide residues were detected in any of the rear beds of the XAD-2 resin tubes, indicating that there was no breakthrough of these pesticide compounds from the front resin bed to the rear, i.e. there was no overloading of the sampling tubes. At least one trip blank accompanied each batch of samples from each site in each year. No pesticides were detected in any of the trip blank samples, laboratory solvent, or tube blanks.

For two samples ("Belly" from Browerville Site E and "Pillow" from Frazee Site A), the starting and ending flow rates differed by ≥25%, and the total sample volume was calculated based on the greater of the two flow rates. This procedure likely overestimates the sample volume and thus provides a lower bound estimate of the airborne pesticide concentration. For four other samples ("Us" and "Salt," Frazee Site A; "Duck," Frazee Site D; and "Ripe," Perham Site A), the power supply to the pump was interrupted during the sample run. For these samples, the sample volume was calculated assuming that the pump had run until the time the next sample was started. This assumption also overestimates the sample volume and thus provides a lower bound estimate of the airborne pesticide concentration. The reported pesticide concentrations for these five samples should therefore be considered as minimum values, and they are marked as such in the tables in **Appendix 1**.

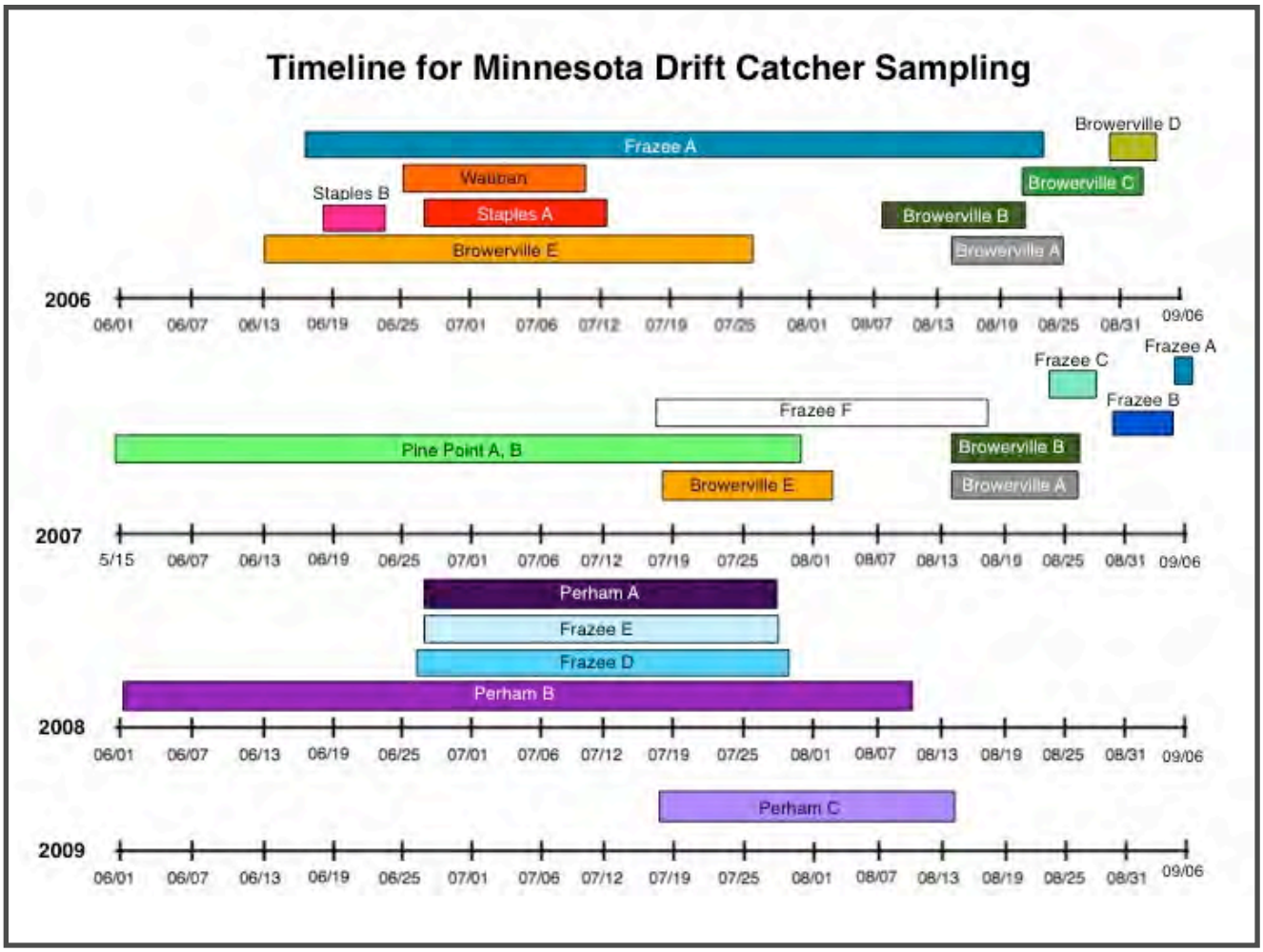



**Figure 9:** Timeline for Minnesota sampling between 2006 and 2009. Over the four-year period, samples were taken over the entire growing season.

**Table 2: Summary of Chlorothalonil Detections at Sample Sites in Minnesota, 2006–2009**

| Site | 2006 Percent of Samples with Detections, Number Tested, Number Collected | 2006 Time-weighted Average Conc. (ng/m³) | 2006 Maximum Conc. (ng/m³) | 2007 Percent of Samples with Detections, Number Tested, Number Collected | 2007 Time-Weighted Average Conc. (ng/m³) | 2007 Maximum Conc. (ng/m³) | 2008 Percent of Samples with Detections, Number Tested, Number Collected | 2008 Time-Weighted Average Conc. (ng/m³) | 2008 Maximum Conc. (ng/m³) | 2009 Percent of Samples with Detections, Number Tested, Number Collected | 2009 Time-Weighted Average Conc (ng/m³) | 2009 Maximum Conc. (ng/m³) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Browerville Site A | 64% 11, 11 | 7 | 46 | 50% 10, 10 | 8 | 36 | | | | | | |
| Browerville Site B | 100% 14, 14 | 2 | 6 | 0% 10, 10 | 0 | 0 | | | | | | |
| Browerville Site C | 100% 11, 11 | 26 | 65 | | | | | | | | | |
| Browerville Site D | 25%, 4, 4 | 1 | 5 | | | | | | | | | |
| Browerville Site E | 100% 8, 16 | 9 | 29 | 0% 13, 13 | 0 | 0 | | | | | | |
| Frazee Site A | 74% 69, 69 | 22 | 181 | 100% 1, 1 | 26 | 26 | | | | | | |
| Frazee Site B | | | | 100% 3, 3 | 30 | 59 | | | | | | |
| Frazee Site C | | | | 75% 4, 4 | 33 | 38 | | | | | | |
| Frazee Site D | | | | | | | 92% 13, 15 | 11 | 40 | | | |
| Frazee Site E | | | | | | | 45% 11, 16 | 52 | 317 | | | |
| Frazee Site F | | | | 100% 21, 21 | 54 | 190 | | | | | | |
| Perham Site A | | | | | | | 100%, 5, 5 | 11 | 23 | | | |
| Perham Site B | | | | | | | 91% 11, 14 | 41 | 164 | | | |
| Perham Site C | | | | | | | | | | 96% 26, 26 | 9 | 19 |
| Pine Point Site A | | | | 43% 23, 23 | 0.6 | 3 | | | | | | |
| Pine Point Site B | | | | 32% 22, 22 | 2.1 | 27 | | | | | | |
| Staples Site A | 92% 13, 13 | 56 | 197 | | | | | | | | | |
| Staples Site B | 0% 4, 4 | 0 | 0 | | | | | | | | | |
| Waubun | 0% 15, 15 | 0 | 0 | | | | | | | | | |

## Chlorothalonil

Chlorothalonil was detected in 217 (64%) of the 340 samples. Detection limits in the PAN lab changed over the time period of the study, and ranged from 0.55 ng/sample to 15 ng/sample (equivalent to air concentrations of 0.2–5 ng/m$^3$ for a 24-hour sample at a 2.0 L/min flow rate). The commercial laboratory detection limit was 10 ng/sample, corresponding to 3 ng/m$^3$. The maximum level of chlorothalonil found in any sample was 317 ng/m$^3$, from sample "Ten," collected July 25–26, 2008 at Frazee Site E (Table 2). Time-weighted average concentrations at the various sites ranged from 0 to 56 ng/m$^3$, with the highest average level of 56 ng/m$^3$ observed at Staples Site A, from June 27–July 12, 2006. **Figure 10** shows an example of chlorothalonil levels at one site, Frazee Site A in 2006, the site with the most days of continuous sampling. In that year, the nearest potato field was 0.4 miles to the south of the sampling site. Chlorothalonil data for the other sites can be found in the appendices.

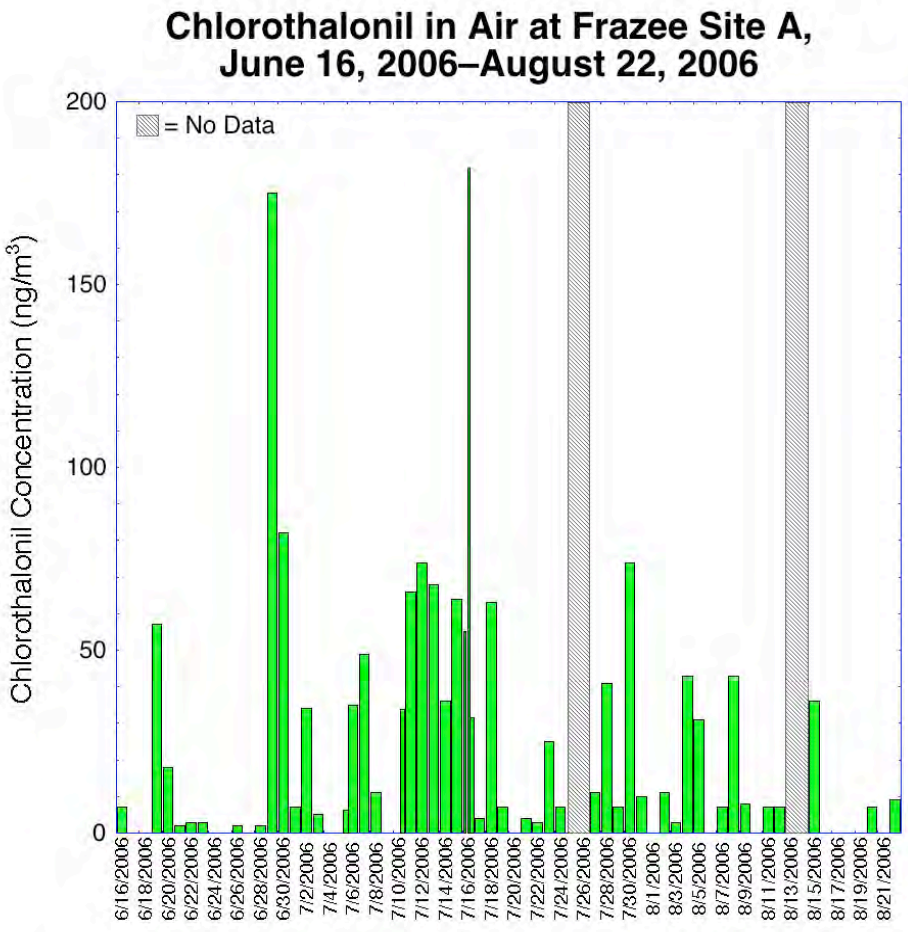



**Figure 10.** Concentrations of chlorothalonil in air at Frazee Site A in the summer of 2006.

## EBDC fungicides

Ethylenebisdithiocarbamate fungicides (e.g. maneb, mancozeb, etc.) are fungicides also used in potato production in the Midwest. These fungicides are much less volatile than chlorothalonil, and therefore unlikely to exhibit significant volatilization drift. Nonetheless, in 2008, a total of ten field samples (selected from Frazee Sites D and E and Perham Site B) were sent to a commercial laboratory for EBDC analysis. None was detected, however the lab's detection limit was rather high: 2.0 µg/sample, equivalent to an air concentration of 690 ng/m$^3$ for a 24-hour sample at a 2.0 L/min flow rate. The sampling and analytical methods used could not detect ethylene thiourea (ETU), the volatile breakdown product of EBDCs. These samples were not analyzed for chlorothalonil.

## Clopyralid and quizalofop-p-ethyl

Clopyralid and quizalofop-p-ethyl are herbicides that were believed to be in use on hybrid poplar trees planted adjacent to Browerville Site E. Therefore in 2006, eight field samples from this site were sent to a commercial laboratory for analysis for these herbicides, neither of which was detected in any sample. The detection limit for clopyralid was 20 ng/sample (equivalent to an air concentration of 7 ng/m$^3$ for a 24-hour sample at a 2.0 L/min flow rate) and for quizalofop-p-ethyl was 50 ng/sample (equivalent to an air concentration of 17 ng/m$^3$ for a 24-hour sample at a 2.0 L/min flow rate). These samples were not analyzed for chlorothalonil.

## Other pesticides

Several other pesticides were detected in samples that were analyzed using multi-residue screens. Chlorpyrifos was detected in samples from Browerville Site B (2006) and Perham Site C (2009). Chlorpyrifos is used on a variety of crops, including corn and soybeans, which are grown in these areas. Of the 40 field samples from these sites, 13 (33%) were found to contain chlorpyrifos. The highest level found was 47 ng/m$^3$ (sample "Seat," collected August 12–13, 2009, at Perham Site C), which is 57% of the Reference Exposure Level of 83 ng/m$^3$, calculated from the proposed Human Equivalent Concentration in U.S. EPA's 2011 Human Health Risk Assessment.[11] The time-weighted average concentrations at these sites was 2 ng/m$^3$ (Perham Site C, July 7–August 13, 2009) and 3 ng/m$^3$ (Browerville Site B, August 7–21, 2006).

The herbicide 2,4-dichlorophenoxy acetic acid ethylhexyl ester (2,4-D) was found in samples from three sites in 2008: Frazee Sites D and E and Perham Site A. Of the 29 field samples from these sites, 2,4-D was detected in 21 (72%). Time-weighted average concentrations at the sites ranged from 7 to 17 ng/m$^3$, and the maximum concentration observed was 115 ng/m$^3$ (Sample "Mud", collected at Site Frazee D on July 19–20, 2008), which is less than 0.1 percent of the Reference Exposure Level of 422,000 ng/m$^3$, calculated from the oral NOAEL in U.S. EPA's 2005 RED.[12] The detection limit for 2,4-D was 8 ng/sample (equivalent to an air concentration of 3 ng/m$^3$ for a 24-hour sample at a 2.0 L/min flow rate).

The fungicide pentachloronitrobenzene (PCNB) was detected in eight of the 14 samples (57%) from Browerville Site B in 2006. The detection limit for PCNB was 1 ng/sample (equivalent to an air concentration of 0.4 ng/m$^3$ for a 24-hour sample at a 2.0 L/min flow rate). The maximum detection was 9 ng/m$^3$ (sample "Gem," August 7–8, 2006), which is 0.5% of the Reference Exposure Level of 1,690 ng/m$^3$, calculated from the oral NOAEL in U.S. EPA's 2006 RED.[13] The time-weighted-average concentration was 2 ng/m$^3$.

A total of 42 samples (12% of the total) were found to contain more than one pesticide, with seven of these samples (2.1%) containing chlorothalonil, PCNB and chlorpyrifos and ten samples (2.9%) containing chlorothalonil and pendimethalin.

## Discussion

The results of the present study are generally consistent with the results of previous monitoring studies. Comparison of the chlorothalonil concentrations measured in Minnesota with those measured by the California Air Resources Board (ARB) near an application site indicates that the highest level observed in Minnesota is 43% of the peak concentration observed within 60 — 100 feet of an application, but the concentrations at the different sites are on the same order of magnitude. Time-weighted average concentrations are in the range of or higher than those observed in ARB's ambient air monitoring studies with 24-hour samples and in a Canadian study. Levels observed at some sites (Frazee Sites A, E, and F; Staples Site A; and Perham Site B) are more in the range of the concentrations observed by ARB in the application site monitoring study and at the farm sites in Canada. None of the concentrations in the Minnesota study were as high as those observed in PAN's Florida study, probably because the sampling sites were closer to fields in Florida. These studies are discussed in detail below.

Comparison of measured levels of chlorothalonil with levels of concern derived from U.S. EPA and California DPR risk assessments is complicated by the fact that there is wide disagreement between CA DPR and U.S. EPA on what the level of concern for inhalation exposures should be, primarily because no low-dose inhalation exposure studies have been conducted. We discuss the various endpoints and their limitations below.

### Comparison of Minnesota results to previous air monitoring studies

Several other air monitoring studies have been conducted that provide information on both near-field and average ambient concentrations of chlorothalonil in areas of high use. We summarize these studies here.

As part of the implementation of the California Air Toxics Act, the California Air Resources Board (ARB) has conducted air monitoring studies for a number of different pesticides adjacent to application sites, which provide information on acute (short-term) exposure in these settings.[14] In these application-site monitoring studies, air sampling stations are generally set up between 25 and 500 feet from the borders of a field that will be treated. All pesticide applications monitored by the ARB were carried out according to label instructions. Therefore, their monitoring results represent a best-case scenario in terms of applicator compliance with best practices to reduce drift.

In September 2002, ARB conducted an application site monitoring study for chlorothalonil and methamidaphos. The site was a 20-acre tomato field in San Joaquin County.[6] The results indicate that chlorothalonil concentrations immediately adjacent to an application can remain above 100 ng/m$^3$ for several days after an application.

**Figure 11** shows the results of the ARB study in terms of air concentration of chlorothalonil over time at sampling sites located 60–100 feet from each of the four sides and four corners of the field. The concentration of chlorothalonil in the air peaked at 740 ng/m$^3$ at the sampling site located due east of the field. This peak occurred during the 2.8 hour sampling period that started 3.1 hours after the application ended. Several studies have been done to measure

ambient air concentrations of chlorothalonil in agricultural areas. These data are summarized in **Figure 12**; the individual studies are discussed below.

ARB measured seasonal concentrations of chlorothalonil in ambient air by deploying monitoring stations in populated areas somewhat distant from application sites, but in regions of high use. In 2003, ARB monitored ambient air for chlorothalonil at six sites in Fresno County in the month of highest chlorothalonil use for the county. Chlorothalonil was detected in 56% of the 142 samples collected, with a maximum concentration of 14 ng/$m^3$ and mean concentrations for the six sites ranging from 0.39 to 2.2 ng/$m^3$.[15] In the summer of 2000, ARB also monitored for chlorothalonil as part of its multi-pesticide ambient air monitoring study in Lompoc. In this study, chlorothalonil was detected in 17% of samples. The highest 14-day average concentration was 3.3 ng/$m^3$ and the highest 90-day average concentration was "trace", or the method detection limit of 1.6 ng/$m^3$.[16] In 2006, DPR and ARB conducted a year-long multi-pesticide air monitoring study in Parlier. With a limit of quantitation for chlorothalonil of 92.6 ng/$m^3$, the study was relatively insensitive for the fungicide; nevertheless, it was detected in 4% of 468 samples. The maximum observed value was "trace," or the method detection limit of 92.6 ng/$m^3$.[17]

In a 2007 PAN study, chlorothalonil was detected in the air adjacent to an elementary school in Hastings, Florida.[18] Chlorothalonil was detected in 85% of the 39 samples, with 77% of the samples containing concentrations above the LOQ of 36 ng per sample (equivalent to an air concentration of 12 ng/$m^3$ for a 24 hour sample) and 8% of the samples containing concentrations between the MDL of 7.1 ng per sample (equivalent to an air concentration of 2.5 ng/$m^3$ for a 24 hour sample) and the LOQ. The average sample concentration for the site was 107 ng/$m^3$, with highest concentration reaching 555 ng/$m^3$ on October 24, 2007.

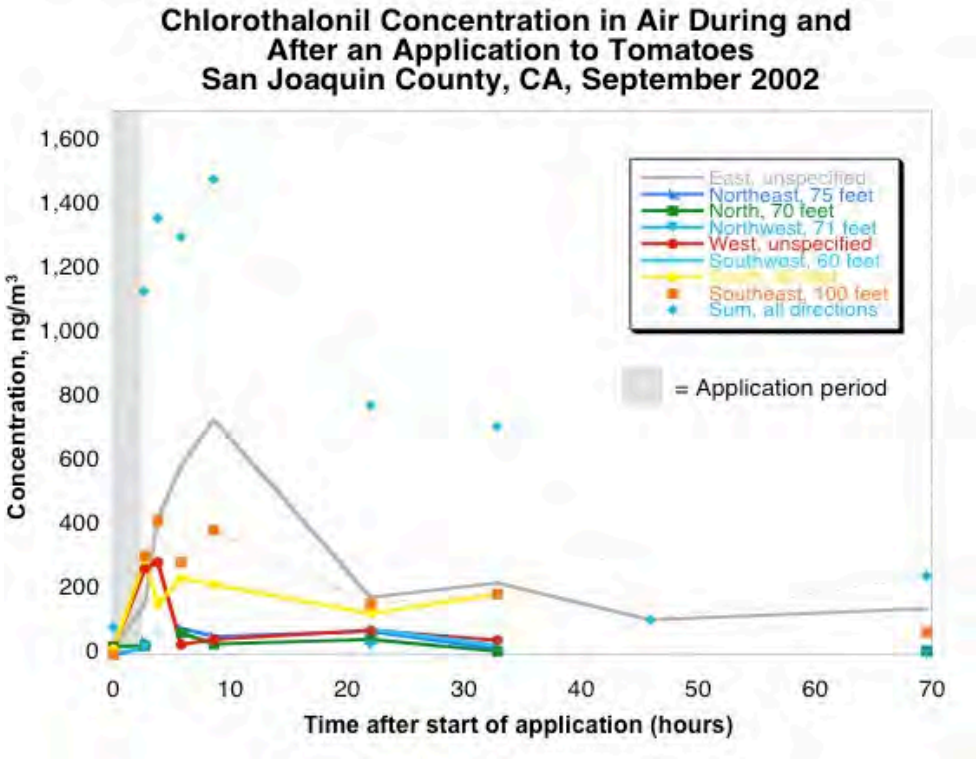



**Figure 11:** Chlorothalonil concentrations in air during and after an application to a tomato field. Concentrations peaked a few hours after the application ended, and level were still in excess of 100 ng/m$^3$ for several days after the application.

Researchers with the Canadian government have also studied chlorothalonil levels in ambient air in urban and rural sites on Prince Edward Island in 1998 and 1999 during the potato-growing season.[19] The three rural sampling stations were on farms and all were within 100 m of residences. Maximum and mean chlorothalonil concentrations at these sites were 45–636 ng/m$^3$ and 22–284 ng/m$^3$, respectively. At the urban site, Abram Village, which is "surrounded primarily with forested lands," the maximum and average chlorothalonil concentrations were 3.9 ng/m$^3$ and 2.1 ng/m$^3$, respectively. Chlorothalonil was detected in 100% of the samples from both the urban and rural sites.

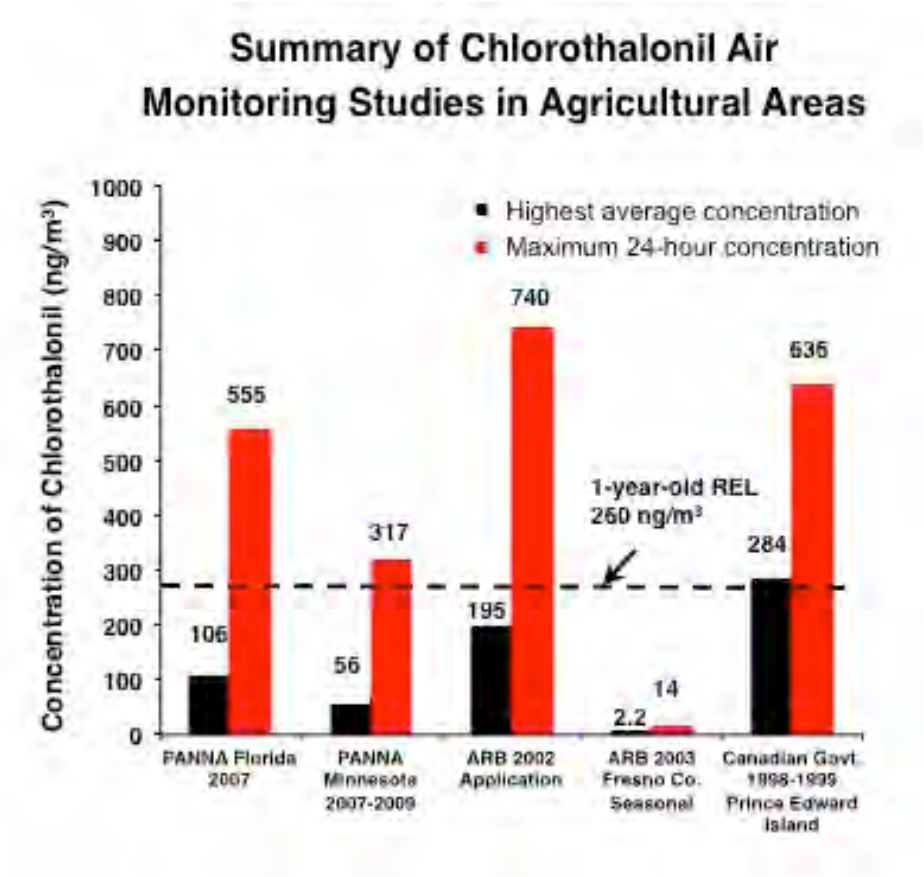



**Figure 12:** Chlorothalonil concentrations in ambient air in different locations during seasons of high chlorothalonil use. The lowest comparable short-term Reference Exposure Level from U.S. EPA's Registration Review Scoping document (see Table 3 below) is shown for reference, but a definitive REL based solely on inhalation toxicity data has not yet been determined.

## Comparison of measured chlorothalonil concentrations to levels of concern

In order to assess the potential for harm, we normally compare the measured concentrations to levels of concern for acute and short-term exposure derived from toxicity data presented in risk assessments by the U.S. EPA, the California Department of Pesticide Regulation (DPR), and the California Office of Environmental Health Hazard Assessment. In theory, these levels of concern represent the air concentration in micrograms of pesticide per cubic meter of air ($\mu g/m^3$) equivalent to a dose in milligrams of pesticide per kilogram of body weight (mg/kg) below which the risk of adverse effects for a one-year-old child is anticipated to be negligible, assuming exposure to chlorothalonil alone. A comprehensive discussion of how to interpret air monitoring results is presented in **Appendix 2**.

For chlorothalonil, this comparison is complicated by the fact that there is wide disagreement between CA DPR and U.S. EPA on what the level of concern for inhalation exposures should be, primarily because no low-dose inhalation exposure studies have been conducted (i.e., studies that would permit determination of a No Observed Adverse Effect Level or NOAEL). Even within

a single agency at different points in time, there is little agreement. **Table 3** provides a comparison of the different endpoints used by U.S. EPA and CA DPR in their various risk assessments. We converted U.S. EPA's NOAELs or Human Equivalent Concentration to RELs for a one-year-old child. DPR's Screening Levels are equivalent to RELs for a one-year-old child.

**Table 3: Levels of Concern for Chlorothalonil**

| Agency | Short-term REL for 1-yr-old ($ng/m^3$) | Comments | Reference |
|---|---|---|---|
| **US EPA** | 34,000 | NOAEL = 2.0 mg/kg-day, oral dosing; UF = 100 | 1999 RED [20] |
| **US EPA** | 52,000 | NOAEL = 30.8 mg/kg-day, oral dosing; UF = 1,000 | 2007 Tolerance [21] |
| **US EPA** | 51,000 | NOAEL = 3.0 mg/kg-day, oral dosing; UF = 100 | 2008 Tolerance [22] |
| **US EPA** | 260 | HEC = 0.00006 mg/L, acute inhalation dosing; UF = 1,000 (including proposed FQPA SF = 30) | 2012 Registration Review Scoping Document[25] |
| **CA DPR** | 560 | LOAEL = 0.056 mg/kg-day, acute inhalation dosing; UF = 100 | 2003 Lompoc Screening Levels[16] |
| **CA DPR** | 34,000 | NOAEL = 3.0 mg/kg-day, oral dosing; UF = 100 | 2007 Parlier Screening Levels[17] |

NOAEL= No observed adverse effect level; U.S. EPA and CA DPR use different methods for converting animal NOAELs into human equivalent concentrations, hence the difference between two RELs based on the same endpoint.
UF= uncertainty factor
HEC = Human Equivalent Concentration, which accounts for differences in exposure between humans and laboratory animals.
LOAEL = Lowest observed adverse effect level

The state of California evaluated a number of acute inhalation studies in its review of chlorothalonil.[23] Adverse effects were observed at every dose level tested in every acute inhalation study identified by the state, where mortality of the animals was a common endpoint, even in the lowest dose studies at concentrations of 2,000,000 $ng/m^3$. These studies were conducted on dust or liquid aerosols, which do not penetrate the lungs as deeply as vapor-phase chlorothalonil. None of the studies described in the DPR Risk Characterization document were conducted using a dose range that is comparable to the exposures observed in this study.

Despite the substantial dependence of toxicity on exposure route, U.S. EPA's current risk assessment uses data from an oral study to assess the risk associated with inhalation of chlorothalonil. However, a U.S. EPA Scientific Advisory Panel in 2009 recommended against making this type of oral-to-inhalation extrapolation because of substantial differences in toxic effects by different exposure routes.[24] In the March 28, 2012, Human Health Scoping Document for the Registration Review of chlorothalonil,[25] U.S. EPA recognizes this issue and proposes significant changes to the chlorothalonil risk assessment:

> The oral and inhalation routes of exposure are of the most toxicological concern with chlorothalonil. Based on acute toxicity studies, chlorothalonil is highly toxic via the inhalation route of exposure (Category I). There was a high level of lethality reported in the critical acute inhalation toxicity study ($LC_{50}$ =0.032 [M] and 0.013 [F] mgIL). RAB1, in conjunction with the HED Science Advisory

> Council for Toxicology (ToxSAC), believes that using any oral endpoint may underestimate risk via the inhalation route. The decision was based on the low fraction of the administered dose that was absorbed through the oral route (estimated at 14–20%), which may underestimate toxicity at a higher absorbed fraction (bioavailability) through the inhalation pathway. The lack of a no-observed adverse-effect level (NOAEL) in several acute inhalation toxicity studies carried out with technical-grade chlorothalonil or end-use product formulations is also a concern. Clinical signs consistent with respiratory-tract irritation (i.e., portal-of-entry effects) including nasal discharge, gasping, decreased activity, ptosis, and lethargy, were reported at all exposure concentrations tested across several acute inhalation toxicity studies for chlorothalonil. The effects of short- and intermediate-term inhalation exposures (portal-of-entry or systemic) have not been studied. In the absence of such information, HED recommends that the lowest-observed adverse-effect level (LOAEL) from the critical acute inhalation toxicity study with appropriate uncertainty factors (UFs) be used as the point of departure (POD) to assess inhalation risks (acute, short-, and intermediate-term).

Indeed, the Agency proposes to use the LOAEL from the acute inhalation study to give a Human Equivalent Concentration (HEC) of 0.00006 mg/L, which is then modified with an interspecies uncertainty factor of 3.3, an intraspecies uncertainty factor of 10, and Food Quality Protection Act (FQPA) safety factors of three (for acute exposures) and 30 (for seasonal exposures) to account for uncertainties regarding inhalation toxicity. This produces a REL of 260 ng/$m^3$ for short- and intermediate-term exposures. Additionally, U.S. EPA will be requiring registrants to submit additional data on inhalation toxicity.

> "The Agency anticipates that it may set the FQPA safety factor at 3X for acute and 30X for repeated residential inhalation exposure scenarios for registration review due to uncertainty regarding inhalation toxicity. The Agency anticipates re-evaluating the FQPA Safety Factor based upon submission of anticipated toxicity studies including inhalation, acute neurotoxicity, and immunotoxicity studies."

Our assessment is that the oral studies used as the basis of U.S. EPA's and DPR's current inhalation reference concentrations do not adequately reflect the inhalation toxicity of chlorothalonil, and the available high-dose inhalation studies are inadequate for the assessment of potential effects at lower doses. The development of a proper evaluation of the inhalation toxicity of chlorothalonil should be a high priority for U.S. EPA and the California Department of Pesticide Regulation, and should include evaluation of a valid inhalation toxicity study designed to capture NOAELs at low doses.

#### Chlorothalonil—Non-cancer risk

Considered individually or as time-weighted averages, none of the chlorothalonil levels observed in this study exceed RELs based on current EPA or DPR screening level for chlorothalonil. However, as discussed above, we have little confidence that the levels of concern as determined by EPA are health protective. Without having appropriate levels of concern for chronic and sub-chronic non-cancer endpoints, we cannot speculate about the non-cancer risks posed by the ubiquitous, long-term inhalation exposure to chlorothalonil documented in this study.

### Chlorothalonil—Cancer risk

Chlorothalonil is classified by the U.S. EPA as Likely to Be a Human Carcinogen (formerly B2, Probable carcinogen).[22] Because the genetic toxicity testing indicates that chlorothalonil is not a mutagen, the U.S. EPA assumes a non-linear mode of action for chlorothalonil carcinogenesis; however, the state of California Office of Environmental Health Hazard Assessment (OEHHA) has adopted a linearized multi-stage procedure for all Proposition 65 carcinogens, utilizing cancer potency factors (Q*) to estimate population level cancer risks.[26]

We used the OEHHA method to estimate lifetime cancer risks based on the ambient chlorothalonil levels observed in this study at Frazee Site A, the site for which the maximum number of samples was available, and the cancer potency factor (Q*) of 0.0076 $(mg/kg\text{-}day)^{-1}$ used in U.S. EPA's 1999 RED.[20] The lifetime cancer risk is defined as the estimated number of additional cancer cases above a risk of one cancer in one million people. Lifetime cancer risks exceeding one in one million represent risks of concern. In the present study, the average chlorothalonil concentration from June 16 to August 22 was 22 $ng/m^3$. Thus, the lifetime cancer risk was calculated assuming an exposure scenario of 22 $ng/m^3$ per day for 77 days each year, giving a lifetime cancer risk of 0.01 excess cancers per million people. **Table 4** summarizes the calculation, which does not exceed the level of concern of one excess cancer per one million people, assuming the oral study on which the cancer potency is based is a valid measure for inhalation exposure. See the **Calculations** section for full details.

The TWA concentration of 22 $ng/m^3$ translates to a daily dose for a one-year-old child breathing 4.5 $m^3$/day of 0.1 µg/day. Comparison of this value to the California Office of Environmental Health Hazard Assessment's calculated No Significant Risk Level (NSRL) of 41 µg/day provided the same result—a concentration below levels of concern for cancer risk.[27]

**Table 4: Cancer Risk Estimate for Chlorothalonil Exposure**

| Parameter | Chlorothalonil |
|---|---|
| **Average concentration during monitoring period ($ng/m^3$)** | 22 |
| **Exposure frequency as percent of a year** | 21.1% |
| **Average annual concentration ($ng/m^3$)** | 4.64 |
| **Annual exposure[a] (mg/kg-day)** | $1.3x10^{-6}$ |
| **Cancer potency factor, Q* $(mg/kg\text{-}day)^{-1}$** | 0.00766 |
| **Lifetime Cancer Risk (excess cancers per million people)** | 0.01 |

[a]For an adult breathing rate of 0.28 $m^3$ per kilogram of body weight per day, representing the predominant breathing rate for a 70-year life span.

In addition to the carcinogenic effects of chlorothalonil itself, contaminants are also of concern. Hexachlorobenzene (HCB), an impurity in chlorothalonil, is also a B2, probable carcinogen and a persistent organic pollutant whose production and use is banned globally under the Stockholm Convention. HCB is a more potent carcinogen than chlorothalonil by a factor of approximately 1,000; however, the concentration of the compound in chlorothalonil-containing products is required by U.S. EPA to be less than 40 ppm (0.004%). U.S. EPA has determined that exposure to HCB via the dietary route is of concern for crops treated with chlorothalonil. There is no direct translation from dietary to inhalation risks. The presence of HCB in the air may be of concern, considering that HCB has a slightly higher vapor pressure than chlorothalonil; however, we did not analyze for HCB in the air samples taken.

## Health effects of pesticides detected in Minnesota

### Chlorothalonil

Chlorothalonil is a broad-spectrum, non-systemic fungicide, widely used in vegetable, field, and ornamental crops, with an estimated 10–14 million pounds used in 2007.[28] It is also used as a wood preservative, anti-mold and anti-mildew agent in paints and coatings, a bactericide, algaecide, insecticide, and acaricide. Its mechanism of action as an anti-fungal agent is by disrupting sulfur-containing enzymes and disrupting energy production in the fungal organism.

Chlorothalonil is not acutely toxic when ingested in a single dose, and U.S. EPA classifies it as "slightly toxic to non-toxic" (Toxicity Category IV) based on an oral $LD_{50}$ in rats of >10,000 mg/kg.[20] In rats, symptoms of exposure to high doses include "lacrimation (watering eyes), dyspnea (shortness of breath), vocalization, ataxia (uncoordinated movements) and tremors." At lower doses over longer time periods, chlorothalonil damages the kidney tubules and the forestomach of the rat. Increases in relative kidney weights, gastritis, decreases in body weight and food consumption for males and females, and changes in enzyme levels, and urinary parameters were observed at all dose levels tested. With chronic dosing, chlorothalonil causes renal tubular cell adenomas/carcinomas.[20] In rats, symptoms of high-dose acute inhalation exposure included "respiratory dysfunction; labored breathing; gasping; excessive ocular nasal and oral secretions; eyes partially and completely closed; decreased activity; wet rales; and dry rales."

In humans, there are reports of allergic reactions to chlorothalonil following both single and prolonged exposures. The flagship case of severe reaction to chlorothalonil is that of an Army Lieutenant who, after playing golf on a course that had been treated with chlorothalonil in the week prior, developed a fever and headache, which progressed to blistered skin, aspiration pneumonia, kidney failure, and ultimately death. Military pathologists concluded that a reaction to chlorothalonil was the cause.[29] One study reported cases of occupational asthma due to repeated exposure to powdered chlorothalonil, indicating that it "can induce specific immunological reactions in the airways as well as skin."[30] Many other accounts of repeated exposures to chlorothalonil report increased sensitivity and allergic reactions to the chemical as well.[31]

### Chlorpyrifos

Chlorpyrifos is an organophosphate insecticide first registered in the United States in 1965. Currently made by Dow AgroSciences under the trade names Dursban and Lorsban, approximately 8–11 million pounds of the active ingredient are used annually in the U.S., with

corn accounting for approximately half of the use.[28] Chlorpyrifos is also applied to a wide variety of fruits, vegetables, and tree nuts, is used as a mosquitocide, on golf courses, and as a wood treatment. It is applied using an aerial or groundboom method, or sprayed directly onto the plant using a backpack or hand-held device.[11] In a growing body of epidemiology studies, chlorpyrifos has shown to adversely affect human health. Three recent studies link prenatal chlorpyrifos exposure to a reduction in full-scale IQ and working memory,[32] poorer processing speed, verbal comprehension, perceptual reasoning,[33] and negatively impacted cognitive development.[34] These findings build on a previous study showing a significant relationship between prenatal chlorpyrifos exposure and an increased occurrence of attention problems, attention-deficit/hyperactivity disorder, and other developmental disorders.[35] Chlorpyrifos acts as a cholinesterase inhibitor—it over-stimulates the nervous system, leading to nausea, dizziness, and confusion. At high exposure rates, respiratory paralysis and death can occur.[11]

### Pendimethalin

Pendimethalin was first registered in the U.S. in 1972 and is an herbicide used on broadleaf and grassy weeds in crop and non-crop areas, as well as residential lawns and ornamentals. It is applied by a variety of methods, including broadcast, chemigation, conservation tillage, containerized plant treatment, soil incorporation, and directed spray. Pendimethalin has been shown to be of low acute toxicity in laboratory animal studies. The thyroid is a target organ, and chronic exposure causes an imbalance in thyroid hormones, increased thyroid weight, microscopic thyroid lesions and thyroid tumors. t has been classified as a Group C, possible human carcinogen by U.S. EPA. U.S. EPA requires use of the Food Quality Protection Act Safety Factor of 10, based on their determination that pendimethalin may cause disruption in the endocrine system. There is concern that perturbation of thyroid homeostasis may lead to hypothyroidism and possibly result in adverse effects on the developing nervous system in the developing fetus. Consequently, EPA has recommended that the manufacturer submit a developmental thyroid assay to evaluate the impact of pendimethalin on thyroid hormones, structure, and/or thyroid hormone homeostasis during fetal development.[36]

### Pentachloronitrobenzene (PCNB)

Pentachloronitrobenzene (PCNB), also called quintozene, is an organochlorine fungicide used largely on cotton and potato fields. It was first registered in 1964, and in 2006 the EPA estimated its annual usage to be between 700,000 and 1,000,000 lbs/year.[13] PCNB has a high persistence in soil, and it is believed that uptake of its residues by plants may continue for several years after the initial pesticide application. PCNB is included in the Hazardous Constituents List of the Resource Conservation and Recovery Act, is considered a priority pollutant by the Clean Water Act, is listed as a having high acute toxicity under the National Institute for Occupational Safety and Health's Registry of Toxic Effects of Chemical Substances, and is identified as a carcinogen by the EPA's Community Advisory Group.[13] Exposure to PCNB adversely affects the central nervous system, liver, and kidneys. PCNB has been shown to cause tissue lesions, and have toxic effects on human reproduction.[13] Approximately 3% of PCNB applied to the soil degrades to pentachlorobenzene (PeCB), a persistent organic pollutant whose use and production is banned globally under the Stockholm Convention.[37] PeCB is highly toxic to fish and other aquatic organisms, bioaccumulates, and resists degradation in the environment.[38]

**2,4-D Ethyl hexyl ester**

The herbicide 2, 4-Dichlorophenoxyacetic acid (2,4-D) and its salts and esters are selective herbicides that have been in use since the 1940s. Forty-six million pounds of 2,4-D and its salts and esters are used annually—two thirds for agricultural and one third for non-agricultural purposes—making this the world's most widely used herbicide, and the third most frequently applied herbicide in North America.[12] The ethyl hexyl ester is sold in the U.S. under the trade names Killex, Weed B Gon Max, and Tri-kill. Applications sites include field, fruit, and vegetable crops, and home lawns. In 2005, two thirds of annual domestic usage was in agriculture, and was applied predominantly in the Midwest, Great Plains, and Northwestern United States. In acid or salt form, 2,4-D is a severe eye irritant; generally low systemic toxicity is observed by the oral route, but inhalation data are lacking. Excretion of the chemical is fairly rapid until the kidneys' capacity to do so is exceeded. Above that dose level, the primary target organs are the eye, thyroid, kidney, adrenals, and ovaries/testes.

# Calculations

## Air concentrations from gas chromatograph (GC) results

Pesticide concentrations in air were calculated from the analytical results obtained with the gas chromatograph as shown in equation (1):

$$\text{Air concentration, ng/m}^3 = \frac{\text{Extract concentration, ng/}\mu\text{L} \times \text{Solvent volume, } \mu\text{L}}{\text{volume of air sampled, m}^3} \quad (1)$$

## Calculation of reference exposure levels (RELs) from reference doses

The U.S. EPA estimates the "acceptable" dietary exposure to a chemical for a human by dividing a No Observed Adverse Effect Level (NOAEL, in mg/kg-day) from an animal study by two or more uncertainty factors. Similarly, calculation of the "acceptable" air concentration of a chemical for a human also starts with a NOAEL from animal study. Since the toxicity of chemicals can vary greatly depending on exposure route, whenever possible inhalation levels of concern should be based on NOAELs derived from inhalation studies.[24] Unfortunately, such studies are relatively rare and, often, regulatory agencies instead rely on oral studies to assess inhalation risk. In general once an appropriate NOAEL has been identified, it is modified by a series of uncertainty factors. These are:

- An interspecies factor ($UF_{inter}$) of 10 to allow for the differences between laboratory animals and humans. For example, if the dose that results in no observed effect (the NOAEL) in a rat study were 3 mg/kg-day and no human studies on acute toxicity were available, the "acceptable" dose for a human would be lowered to 0.3 mg/kg-day. In practice, the relative sensitivity of laboratory animals compared to humans is different for each chemical. In cases where both human data and rat data are available, this factor ranges from humans being 1,000 times more sensitive than rats to one tenth as sensitive.[39] The factor of ten—to allow for ten times greater human vulnerability—is the most commonly chosen, but is not sufficiently protective for all chemicals.
- An intraspecies factor ($UF_{intra}$) of 10 to allow for the differences between different human individuals. Genetic differences exist in humans' ability to detoxify and eliminate toxic substances. A good example is the 80-year-old who has smoked two packs of cigarettes a day for 60 years and escapes lung cancer compared to the 25-year-old who acquires multiple chemical sensitivity after a single exposure to a toxic substance. The intraspecies uncertainty factor attempts to take these differences into account. However, the genetic variability in humans' ability to detoxify pesticides is known to exceed a factor of 10 in at least one situation.[46]
- Other uncertainty factors ($UF_{other}$) may also apply. This is often the case when an inhalation NOAEL is not available because the pesticide is toxic to the test-animals at all dose levels tested. In such a case, the lowest dose tested—the Lowest Observed Adverse Effect Level (LOAEL)—can be used in place of a NOAEL, but an additional uncertainty factor is required. This additional factor can range from 2 to 10.
- For children, the Federal Food Quality Protection Act (FQPA) requires U.S. EPA to use an additional child uncertainty factor (FQPAF) of 10 to allow for the fact that infants and children are particularly susceptible to toxicants. If additional information is available indicating that children are *not* especially susceptible to toxic effects from the chemical, this uncertainty factor might be reduced to less than 10 and can even be reduced to one,

eliminating it from the calculation. If no data are available on toxic effects that might be specific to children (e.g., developmental neurotoxicity), the law requires the factor of 10 to be used.

In the 2008 Tolerance decision for chlorothalonil, U.S. EPA determined that there is no reason to expect infants or children to be more susceptible than adults, and therefore set the FQPAF to one; however, the Registration Review Scoping Document indicates that inhalation exposures may require an FQPA SF of three to 30.[25]

We refer to the NOAEL modified by the relevant uncertainty factors as an "inhalation reference dose" (iRfD). For adults, acute and sub-chronic iRfDs were obtained by dividing the relevant NOAEL or LOAEL by the intraspecies and interspecies uncertainty factors, as well as any other modifying factors used by the U.S. EPA, as shown in equation (2). The FQPAF was not used, as it only applies to children.

$$\text{Adult iRfD (mg/kg - day)} = \frac{\text{NOAEL or LOAEL (mg/kg - day)}}{\text{UF}_{\text{intra}} \times \text{UF}_{\text{inter}} \times \text{UF}_{\text{other}}} \quad (2)$$

Acute and sub-chronic iRfDs for children were obtained by dividing the NOAEL or LOAEL listed in Table 6 by the intraspecies, interspecies, and any other relevant uncertainty factors, as well as the child uncertainty factor (FQPAF), as shown in equation (3).

$$\text{Child iRfD (mg/kg - day)} = \frac{\text{NOAEL or LOAEL (mg/kg - day)}}{\text{UF}_{\text{intra}} \times \text{UF}_{\text{inter}} \times \text{UF}_{\text{other}} \times \text{FQPAF}} \quad (3)$$

Inhalation reference doses (in units of mg/kg-day) were converted to RELs (air concentrations, with units of ng/m$^3$) using equation (4), where BW and BR are the average body weight and breathing rate of the population in question (70 kg adult male, seven-year-old child, and one-year-old infant). We chose a single point estimate of exposure using exposure parameters previously developed for the three populations (see Table 5).[40] The REL in ng/m$^3$ determined in equation (4) can be thought of as the answer to the following question: For a person to inhale, over the course of 24 hours, a dose equivalent to the iRfD, what would the concentration of the pesticide in the air have to be?

$$\text{REL (ng/m}^3\text{)} = \frac{\text{iRfD (mg/kg - day)} \times \text{BW(kg)} \times 10^6 \text{ng/mg}}{\text{BR (m}^3\text{/day)}} \text{ x } 100\% \quad (4)$$

There are three important assumptions implicit in this conversion. They are:

1. **Physiology.** Body weight and breathing rates vary across the population and average parameters are, of course, dependent on age, as shown in Table 5. As shown in Table 5 below, RELs calculated for one-year-old infants are consistently lower than those calculated for seven-year-olds, and this is due entirely to using reference physiological parameters for infants rather than seven-year-olds.

**Table 5: Exposure Parameters**

| | Body Weight (kg) | Breathing Rate ($m^3$/day) |
|---|---|---|
| Adult male | 70 | 18 |
| One-year-old child | 7.6 | 4.5 |

*Data source:* Reference 40, 47

2. **Absorption.** When the iRfD is derived from oral rather than inhalation data, absorption of the compound via inhalation was assumed to be equivalent to absorption via ingestion, thus the factor of 100%, according to standard U.S. EPA methodology.[41]

3. **Duration.** We assume a 24-h exposure, and use average daily breathing rates, which include periods of inactivity when breathing rates are low (e.g. sleep). Had we assumed a shorter duration of exposure, the calculated RELs would be higher, since in order to inhale the same dose in a shorter amount of time, the airborne pesticide concentration would have to be higher. However in calculations of RELs for durations less than 24-h, care should be taken to use breathing rates appropriate for the exposure scenario under consideration—using daily average breathing rates to calculate a REL for a period of high activity will result in an artificially high result. We have assumed 24-h exposures for several reasons:

   - To avoid the ambiguities in selecting an appropriate breathing rate described above;
   - To facilitate comparison to the levels found in the air samples, which were collected over periods of approximately 24-h (and thus represent average daily concentrations); and
   - To be protective of people who are likely to be exposed for close to 24 hours. Our results indicate that most of the observed pesticides are in the air in the area on most days. Therefore, since the air inside buildings in the area is not pumped in from off-site, it is more reasonable to assume that indoor air concentrations approximate outdoor levels than it is to assume that pesticides do not enter the indoor environment. In other words, exposure is not likely to be limited to only when people are outdoors.

## Estimation of lifetime cancer risks

To estimate the risk of cancer from exposure to a substance over a 70-year lifetime, one must know the following:

- The **average concentration** of the substance in air during the monitoring period.
- The **exposure frequency**, or the fraction of a year in which concentrations are estimated to equal the average concentration measured during the monitoring period.
- The **average annual concentration** of the substance in air, determined from the exposure frequency and the average concentrations observed during the monitoring period.
- The **cancer potency factor, Q***, determined from toxicity studies. For chlorothalonil, a "Probable" carcinogen, U.S. EPA used a Q* of 0.00766 $(mg/kg\text{-}day)^{-1}$.[20]

Details for each calculation are shown below.

#### Estimation of average air concentrations during the application period

The time-weighted average concentration of chlorothalonil measured at Frazee Site A (the location for which the maximum amount of data were available) was 22 ng/m$^3$, for the period from June 16 to August 22, 2006, a period of 77 days.

#### Estimation of exposure frequency

The length of the application season (and hence exposure frequency) for these pesticides in the Frazee area of Minnesota is not precisely known. In these cancer risk calculations we have assumed that exposure is limited to just the portion of the year for which we have data: June 16–August 22 (77 days, 21% of the year). This assumption may underestimate the duration of exposure, and therefore cancer risk, since these pesticides are labeled for repeated use throughout the growing season, and our sampling did not likely bracket the entire season.

#### Estimation of average annual air concentration and exposure

Average annual air concentrations were calculated by multiplying estimated seasonal average air concentrations by the exposure frequency, according to equation (5).

$$\text{Avg. annual conc. (ng/m}^3\text{)} = \text{(Avg. conc. during monitoring period)} \times \text{(Exposure frequency)} \quad (5)$$

Annual exposure was calculated by multiplying the average annual air concentration by the adult inhalation rate of 0.28 m$^3$/kg-day,[40] according to equation (6). This calculation assumes the annual average air concentrations remain at the same level from year to year.

$$\text{Annual exposure (mg/kg - day)} = \text{(Avg. annual conc. (ng/m}^3\text{)} \times 10^{-6}\,\text{mg/ng)} \times \text{(0.28 m}^3\text{/kg - day)} \quad (6)$$

#### Determination of lifetime cancer risks

To obtain the lifetime (70-year) cancer risk, the average annual exposures in mg/kg-day were multiplied by the potency factor (Q*) in (mg/kg/day)$^{-1}$, according to equation (7).

$$\text{Lifetime cancer risk} = \left(\text{Annual exposure (mg/kg - day)}\right) \times \left(Q_1^*\ \text{(mg/kg - day)}^{-1}\right) \quad (7)$$

The lifetime cancer risk is defined as the estimated number of cancer cases above the number considered to be a background rate for a population. Lifetime cancer risks exceeding one in one million represent risks of concern, therefore for convenience the values given in **Table 4** have been multiplied by $1\times10^6$. The resulting cancer risk for chlorothalonil exposures does not exceed the level of concern (i.e., 1.0).

## Method detection limit (MDL)

The method detection limit (MDL) is the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyses of a sample in a given matrix containing the analyte."[42] For air samples, the MDL takes into account the total amount of sampling time, the air flow rate through the sorbent tube, the volume of extraction solvent used to desorb the analyte, and the sensitivity of the instrument used to quantify the amount of analyte in a sample. For this experiment, the MDL was determined for a 24-hour sample taken with a flow rate of 2.00 L/min, and extracted with 2.00 mL of solvent. The sensitivity of the gas chromatograph equipped with an electron capture detector, the Instrument Detection Limit

(IDL), was calculated by determining the standard deviation (σ) of the results of seven sequential injections of a low-level solution of the analyte of interest (0.005 ng/µL for α-endosulfan, 0.01 ng/µL β-endosulfan, 0.01 ng/µL for endosulfan sulfate, 0.05 ng/µL for diazinon, 0.01 ng/µL for chlorothalonil, and 0.005 ng/µL for trifluralin) and multiplying this value times 3.14, the student T value at the 99% confidence interval for seven replicates, as shown in equation (8).

$$\text{IDL (ng/µL)} = 3.14 * \sigma \qquad (8)$$

These parameters were then used to calculate the MDL for the entire method in units of concentration of pesticide in air, e.g. ng/m$^3$. The equation for the MDL calculation is shown in equation (9).

$$\text{MDL (ng/m}^3\text{)} = \frac{(\text{IDL ng/µL}) \times (2{,}000\ \text{µL})}{(2.0\ \text{L/min}) \times (60\ \text{min/h}) \times (24\ \text{h}) \times (1\ \text{m}^3/1000\ \text{L})} \qquad (9)$$

The IDL depends strongly on the injector split ratio employed in the analysis. As indicated in Appendix 13, a variety of split ratios were employed in order to bring the analytes and calibration standards into the linear range of the ECD. The LOQs, IDLs, and MDLs quoted in the body of this text reflect the detection limits of the most sensitive method (lowest split ratio) for each analyte.

The Limit of Quantitation (LOQ) was estimated at five times the MDL.

## Quality Assurance–Quality Control

### Operator training

All Drift Catcher Operators participated in a hands-on training workshop on the operation of the Drift Catcher at which they were provided with a Drift Catcher Users' Manual. They were then tested on their knowledge of the procedures and practices by a PAN scientist. Participants were certified if they could successfully demonstrate:

1. Mastery of the technical set-up and operation of the Drift Catcher
2. Correct use of Sample Log Sheets and Chain of Custody Forms
3. Ability to troubleshoot and solve common operational problems
4. Knowledge of the scientific method

### Sample labels

Sample labels were affixed directly to the sorbent tubes and to the corresponding sample log sheets prior to the start of sampling. The following information was contained on the labels: Sample ID, project name, and project date.

## Sample check-in

On arrival in the laboratory, samples were checked into a Sample Log Database organized by project and sampling dates. Sampling dates and times, extraction dates, analysis dates, analytical methods and sample results were all logged in the database. Appendix 8 shows a screen shot of the main Sample Log Database page.

## Leak check

All monitoring equipment was fully leak-checked prior to use by attaching the tubing-manifold combination to a pump generating a positive airflow and testing for leaks at each connection point with a soap solution.

## Flow calibration

Rotameters used in the field to determine flow rates were calibrated using an Aalborg mass flow meter, Model No. GFM17A-VADL2-A0A with totalizer attachment TOT-10-0C. All rotameters used in this experiment deviated less than 5% (the rated accuracy for these rotameters) from the mass flow meter readings.

## Trip blanks

A pair of trip blank tubes was prepared for each sample set at each location for each sampling period. These tubes were stored and transported with the samples from that location, and one from each pair was processed and analyzed as part of the batch on arrival in the lab. No pesticide residues were detected in the trip blanks. These data are shown in Appendix 1 tables.

## Lab blank

With each set of tubes analyzed, one blank tube of the same lot number as that of the tubes used in the experiment was processed and analyzed according to the methods used for the samples. No pesticide residues were detected in the lab blanks.

## Solvent blanks

A sample of the solvent used for extraction was analyzed with each batch of samples to check for possible impurities in the solvent. No pesticide residues were detected in any of the solvent blanks.

## Instrumental QA/QC

Quantitation was conducted using an electron capture detector (ECD) calibrated with a set of at least five standards encompassing the linear range of the detector. Positive identification of each pesticide was established by mass spectrometry, as well as by comparison of retention times between two different columns. The linearity of the standard curve was confirmed by inspection and evaluation of the regression coefficient, which was required to be at least 0.99. A new set of standards was analyzed for each 30–40 samples, with a mid-level calibration verification standard analyzed every 10$^{th}$ sample. See Appendix 9 for detailed instrument parameters.

# Appendices

## Appendix 1: Data Tables

Notes for all data tables that follow:
a: analysis performed by commercial lab. Unless otherwise noted, the analysis was specific to the chemical named in the table, i.e. a multi-residue screen was not used.
b: chlorothalonil < reporting limit (commercial lab)
c: chlorothalonil < MDL
d: chlorothalonil < LOQ
e: chlorpyrifos < MDL
f: chlorpyrifos < LOQ
g: PCNB < MDL
h: PCNB < LOQ
i: clopyralid < reporting limit (commercial lab)
j: quizalofop-p-ethyl < reporting limit (commercial lab)
k: EBDCs < reporting limit (commercial lab)
l: 2,4-D < MDL
m: 2,4-D < LOQ
n: analysis performed by commercial lab using a multi-residue screen.
o: pendimethalin < MDL
p: pendimethalin < LOQ

MV = minimum value (see text)
MDL = method detection limit
LOQ = limit of quantitation
EBDC = ethylene bis(dithiocarbamate), a degradation product of maneb and mancozeb

**Table A1: Pesticide Concentration in the Air at Browerville Site A, August 14–25, 2006, and August 14–26, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration (ng/ $m^3$) | Notes |
|---|---|---|---|---|---|
| **2006** | | | | | |
| Elm | 8/14/2006 | - | - | 0 | Trip Blank, c |
| Fame | 8/14/2006 | 1282 | 2.60 | 46 | |
| Ghost | 8/15/2006 | 1467 | 2.97 | 3 | d |
| Soil | 8/16/2006 | 1414 | 2.90 | 0 | c |
| Letter | 8/17/2006 | 1452 | 2.83 | 3 | d |
| Money | 8/18/2006 | 1489 | 2.94 | 6 | |
| Oval | 8/19/2006 | 1367 | 2.60 | 12 | |
| Jig | 8/20/2006 | 1417 | 2.83 | 5 | |
| Jet | 8/21/2006 | 1424 | 2.74 | 9 | |
| Cot | 8/22/2006 | 1394 | 2.78 | 0 | c |
| Gruel | 8/23/2006 | 1459 | 2.89 | 0 | c |
| Palm | 8/24/2006 | 1443 | 2.81 | 0 | c |
| **2007** | | | | | |
| Bar | 8/14/2007 | 1173 | 2.35 | 0 | a, b |
| Flip | 8/15/2007 | - | - | 0 | Trip Blank, a, b |
| Willow | 8/15/2007 | 1305 | 2.58 | 9 | a |
| All | 8/16/2007 | 1449 | 2.83 | 0 | a, b |
| Mitt | 8/17/2007 | 1555 | 3.07 | 0 | a, b |
| Button | 8/20/2007 | 1428 | 2.71 | 0 | a, b |
| City | 8/21/2007 | 1435 | 2.87 | 17 | a |
| Ball | 8/22/2007 | 1445 | 2.85 | 36 | a |
| Tigger | 8/23/2007 | 1420 | 2.77 | 7 | a |
| Yep | 8/24/2007 | 1528 | 3.09 | 0 | a, b |
| Hit | 8/25/2007 | 1415 | 2.76 | 10 | a |

**Table A2: Pesticide Concentration in the Air at Browerville Site B, August 7–21, 2006. and August 14–26, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Chlorpyrifos Concentration ($ng/m^3$) | Pentachloro-nitrobenzene Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|---|
| **2006** | | | | | | | |
| Grub | 8/7/2006 | - | - | 0 | 0 | 0 | Trip Blank, c, e, g |
| Gem | 8/7/2006 | 1306 | 2.51 | 4 | 0 | 9 | e, |
| Cob | 8/8/2006 | 1008 | 2.02 | 4 | 15 | 6 | |
| Ilk | 8/9/2006 | 1397 | 2.79 | 6 | 6 | 3 | |
| Ace | 8/10/2006 | 1448 | 2.89 | 2 | 2 | 0 | f, g |
| Sub | 8/11/2006 | 1444 | 2.88 | 2 | 2 | 0 | f, g |
| Heat | 8/12/2006 | 1398 | 2.79 | 1 | 5 | 2 | d |
| Plum | 8/13/2006 | 1430 | 2.93 | 2 | 2 | 0 | f, g |
| Knot | 8/14/2006 | 1384 | 2.77 | 2 | 2 | 1 | f, g, h |
| Dream | 8/15/2006 | 1463 | 2.93 | 1 | 2 | 3 | c, f |
| Broom | 8/16/2006 | 1417 | 2.83 | 1 | 2 | 1 | c, f, h |
| Post | 8/17/2006 | 1451 | 2.90 | 1 | 2 | 2 | c, f |
| See | 8/18/2006 | 1479 | 2.99 | 1 | 0 | 0 | c, e, g |
| Dot | 8/19/2006 | 1371 | 2.74 | 1 | 0 | 0 | c, e, g |
| Elf | 8/20/2006 | 1464 | 2.93 | 1 | 0 | 0 | c, e, g |
| **2007** | | | | | | | |
| Dark | 8/14/2007 | 1153 | 2.22 | 0 | Not Tested | Not Tested | a, b |
| Field | 8/15/2007 | - | - | 0 | Not Tested | Not Tested | Trip Blank, a, b |
| Oak | 8/15/2007 | 1311 | 2.56 | 0 | Not Tested | Not Tested | a, b |
| Pet | 8/16/2007 | 1448 | 2.82 | 0 | Not Tested | Not Tested | a, b |
| Tunnel | 8/17/2007 | 1568 | 3.21 | 0 | Not Tested | Not Tested | a, b |
| Phone | 8/20/2007 | 1428 | 2.75 | 0 | Not Tested | Not Tested | a, b |
| Chair | 8/21/2007 | 1439 | 2.81 | 0 | Not Tested | Not Tested | a, b |
| Night | 8/22/2007 | 1405 | 2.81 | 0 | Not Tested | Not Tested | a, b |
| Daisy | 8/23/2007 | 1459 | 2.88 | 0 | Not Tested | Not Tested | a, b |
| Nope | 8/24/2007 | 1496 | 3.03 | 0 | Not Tested | Not Tested | a, b |
| Mad | 8/25/2007 | 1378 | 2.72 | 0 | Not Tested | Not Tested | a, b |

**Table A3: Pesticide Concentration in the Air at Browerville Site C, August 21–September 1, 2006**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration (ng/ $m^3$) | Notes |
|---|---|---|---|---|---|
| Feel | 8/21/2006 | - | - | 0 | Trip Blank, c |
| Deep | 8/21/2006 | 1338 | 2.676 | 5 | |
| Real | 8/22/2006 | 1396 | 2.897 | 37 | |
| Kilt | 8/23/2006 | 1437 | 2.802 | 41 | |
| Kit | 8/24/2006 | 1465 | 2.930 | 41 | |
| Toad | 8/25/2006 | 1472 | 2.981 | 10 | |
| Bike | 8/26/2006 | 1387 | 2.774 | 11 | |
| Fairy | 8/27/2006 | 1473 | 2.909 | 17 | |
| Glory | 8/28/2006 | 1409 | 2.818 | 3 | |
| Gross | 8/29/2006 | 1447 | 2.930 | 14 | |
| Gave | 8/30/2006 | 1422 | 2.844 | 42 | |
| Flin | 8/31/2006 | 1427 | 2.854 | 65 | |

**Table A4: Pesticide Concentration in the Air at Browerville Site D, August 28–September 1, 2006**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration (ng/ $m^3$) | Notes |
|---|---|---|---|---|---|
| Met | 8/28/2006 | - | - | 0 | Trip Blank, c |
| Trap | 8/28/2006 | 1410 | 2.82 | 0 | c |
| Chain | 8/29/2006 | 1437 | 2.91 | 0 | c |
| Bet | 8/30/2006 | 1436 | 2.87 | 0 | c |
| Risk | 8/31/2006 | 1430 | 2.75 | 5 | |

**Table A5: Pesticide Concentration in the Air at Browerville Site E, June 13–July 26, 2006, and July 18–August 2, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Clopyralid Concentration ($ng/m^3$) | Quizalofop-P-ethyl Concentration ($ng/m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|---|
| **2006** | | | | | | | |
| Good | 6/13/2006 | 1914 | 3.828 | 0 | 0 | Not Tested | a, i, j |
| Glue | 6/14/2006 | 1457 | 2.841 | 0 | 0 | Not Tested | a, i, j |
| Knife | 6/15/2006 | - | - | 0 | 0 | Not Tested | Trip Blank, a, i, j |
| Sock | 6/15/2006 | 1451 | 2.684 | 0 | 0 | Not Tested | a, i, j |
| Cat | 6/16/2006 | 1282 | 2.628 | 0 | 0 | Not Tested | a, i, j |
| Bread | 6/17/2006 | 1440 | 2.880 | 0 | 0 | Not Tested | a, i, j |
| Horse | 6/18/2006 | 1509 | 2.943 | 0 | 0 | Not Tested | a, i, j |
| Laurel | 6/19/2006 | 1383 | 2.731 | 0 | 0 | Not Tested | a, i, j |
| Apple | 6/20/2006 | 957 | 1.914 | 0 | 0 | Not Tested | a, i, j |
| Lady | 7/18/2006 | 1442 | 2.848 | Not Tested | Not Tested | 29 | |
| Beach | 7/18/2006 | - | - | Not Tested | Not Tested | 0 | Trip Blank, c |
| Belly | 7/19/2006 | 1414 | 2.828 | Not Tested | Not Tested | 8 | MV |
| Happy | 7/20/2006 | 1273 | 2.482 | Not Tested | Not Tested | 4 | |
| Bad | 7/21/2006 | 1452 | 2.904 | Not Tested | Not Tested | 5 | |
| Bug | 7/22/2006 | 1410 | 2.785 | Not Tested | Not Tested | 5 | |
| Great | 7/23/2006 | 1471 | 2.832 | Not Tested | Not Tested | 9 | |
| Charm | 7/24/2006 | 1463 | 2.889 | Not Tested | Not Tested | 5 | |
| Magic | 7/25/2006 | 1419 | 2.838 | Not Tested | Not Tested | 7 | |
| **2007** | | | | | | | |
| Fork | 7/18/2007 | - | - | Not Tested | Not Tested | 0 | Trip Blank, a, b |
| Dance | 7/18/2007 | 1248 | 2.465 | Not Tested | Not Tested | 0 | a, b |
| Pony | 7/19/2007 | 1511 | 2.984 | Not Tested | Not Tested | 0 | a, b |
| George | 7/20/2007 | 1527 | 3.016 | Not Tested | Not Tested | 0 | a, b |
| Book | 7/21/2007 | 1732 | 3.377 | Not Tested | Not Tested | 0 | a, b |
| Rabbit | 7/22/2007 | 1424 | 2.741 | Not Tested | Not Tested | 0 | a, b |
| Alpha | 7/23/2007 | 1336 | 2.538 | Not Tested | Not Tested | 0 | a, b |
| Dad | 7/24/2007 | 1084 | 2.060 | Not Tested | Not Tested | 0 | a, b |
| Card | 7/25/2007 | 1381 | 2.555 | Not Tested | Not Tested | 0 | a, b |
| Green | 7/26/2007 | 1428 | 2.963 | Not Tested | Not Tested | 0 | a, b |
| Yellow | 7/27/2007 | 1471 | 2.942 | Not Tested | Not Tested | 0 | a, b |
| Black | 7/28/2007 | 1258 | 2.422 | Not Tested | Not Tested | 0 | a, b |
| White | 7/30/2007 | 2879 | 5.254 | Not Tested | Not Tested | 0 | a, b |
| Brown | 8/1/2007 | 1376 | 2.786 | Not Tested | Not Tested | 0 | a, b |

**Table A6: Pesticide Concentration in the Air at Frazee Site A, June 16– August 23, 2006, and September 5–6, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| **2006** | | | | | |
| Pillow | 6/16/2006 | 1416 | 2.41 | 7 | MV, c |
| Wire | 6/17/2006 | 1440 | 2.88 | 0 | c |
| Bird | 6/17/2006 | - | - | 0 | Trip Blank, c |
| Red | 6/18/2006 | 1436 | 2.84 | 0 | c |
| Banana | 6/19/2006 | 1530 | 3.06 | 57 | |
| Fred | 6/20/2006 | 1373 | 2.76 | 18 | |
| Omega | 6/21/2006 | 1463 | 2.93 | 2 | d |
| Blue | 6/22/2006 | 1450 | 2.79 | 3 | d |
| Orange | 6/23/2006 | 1402 | 2.73 | 3 | d |
| Song | 6/24/2006 | - | - | 0 | Trip Blank, c |
| Dog | 6/24/2006 | 1278 | 2.52 | 0 | c |
| Them | 6/25/2006 | 1551 | 3.10 | 0 | c |
| Girl | 6/26/2006 | 1472 | 2.94 | 2 | d |
| Pepper | 6/27/2006 | 1401 | 2.78 | 0 | c |
| Snow | 6/28/2006 | 1501 | 3.00 | 2 | d |
| Butter | 6/29/2006 | 1456 | 2.91 | 175 | |
| Us | 6/30/2006 | 611 | 1.22 | 82 | MV, a |
| Mom | 7/1/2006 | - | - | 0 | Trip Blank, a, b |
| Salt | 7/1/2006 | 1370 | 2.74 | 7 | MV |
| Rain | 7/2/2006 | 1493 | 2.72 | 34 | |
| Joker | 7/3/2006 | 1450 | 2.90 | 5 | |
| Shirt | 7/4/2006 | 1261 | 2.54 | 0 | a, b |
| Sky | 7/5/2006 | 290 | 0.58 | 0 | a, b |
| Finger | 7/5/2006 | 1257 | 2.48 | 6 | a |
| Mouse | 7/6/2006 | 1545 | 3.09 | 35 | a |
| Street | 7/7/2006 | 1323 | 2.65 | 49 | a |
| Sunset | 7/7/2006 | - | - | 0 | Trip Blank, a, b |
| Key | 7/8/2006 | 1415 | 2.72 | 11 | a |
| Moon | 7/9/2006 | 1363 | 2.73 | 0 | a, b |
| Car | 7/10/2006 | 241 | 0.48 | 0 | a, b |
| Stone | 7/10/2006 | 237 | 0.47 | 0 | a, b |
| Brick | 7/10/2006 | 257 | 0.51 | 32 | a |
| Wind | 7/10/2006 | 748 | 1.48 | 34 | a |
| Cactus | 7/11/2006 | 1423 | 2.80 | 66 | a |
| Hill | 7/12/2006 | 1417 | 2.83 | 74 | a |
| Board | 7/13/2006 | - | - | 0 | Trip Blank, a, b |
| Earth | 7/13/2006 | 1471 | 2.94 | 68 | a |
| Frog | 7/14/2006 | 1362 | 2.79 | 36 | a |
| Valley | 7/15/2006 | 1513 | 3.29 | 64 | a |
| Cable | 7/16/2006 | 279 | 0.56 | 55 | a |
| Screen | 7/16/2006 | 567 | 1.13 | 181 | a |
| Racoon | 7/16/2006 | 730 | 1.45 | 28 | a |
| **2006 (cont.)** | | | | | |

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Desk | 7/17/2006 | 1365 | 2.62 | 4 | a, b |
| Needle | 7/17/2006 | - | - | 0 | Trip Blank, a, b |
| Toy | 7/18/2006 | 1497 | 2.97 | 63 | a |
| Thread | 7/19/2006 | 1400 | 2.70 | 7 | a |
| Rug | 7/20/2006 | 1332 | 2.66 | 0 | a, b |
| Snake | 7/21/2006 | 1408 | 2.82 | 4 | a |
| Lizard | 7/22/2006 | 1473 | 2.92 | 3 | a |
| Queen | 7/23/2006 | 1430 | 2.80 | 25 | a |
| Prince | 7/24/2006 | 1436 | 2.86 | 7 | a |
| Light | 7/24/2006 | - | - | 0 | Trip Blank, a, b |
| Game | 7/27/2006 | 1411 | 2.77 | 11 | a |
| Desert | 7/28/2006 | 1475 | 2.96 | 41 | a |
| Mole | 7/29/2006 | - | - | 0 | Trip Blank, a, b |
| Spring | 7/29/2006 | 1471 | 2.91 | 7 | a |
| Fall | 7/30/2006 | 1423 | 2.74 | 74 | a |
| Drop | 7/31/2006 | 1475 | 2.88 | 10 | a |
| Petal | 8/1/2006 | 1461 | 2.89 | 0 | a, b |
| Dew | 8/2/2006 | 1407 | 2.81 | 11 | a |
| Sage | 8/3/2006 | 1434 | 2.87 | 3 | a |
| Air | 8/4/2006 | 1416 | 2.79 | 43 | a |
| Pond | 8/5/2006 | 1432 | 2.85 | 31 | a |
| Breeze | 8/6/2006 | 1536 | 3.06 | 0 | a, b |
| Water | 8/6/2006 | - | - | 0 | Trip Blank, a, b |
| Monkey | 8/7/2006 | 1396 | 2.78 | 7 | a |
| Autumn | 8/8/2006 | 1627 | 3.17 | 43 | a |
| Forest | 8/9/2006 | 1269 | 2.60 | 8 | a |
| Ache | 8/10/2006 | 1394 | 2.75 | 0 | a, b |
| Summer | 8/11/2006 | 1479 | 2.85 | 7 | a |
| Candy | 8/12/2006 | 1445 | 2.82 | 7 | a |
| River | 8/15/2006 | 1947 | 3.86 | 36 | a |
| Bulb | 8/16/2006 | 2228 | 4.23 | 0 | a, b |
| Stalk | 8/18/2006 | - | - | 0 | Trip Blank, a, b |
| Wizard | 8/18/2006 | 1452 | 2.94 | 0 | a, b |
| Druid | 8/19/2006 | 1396 | 2.79 | 0 | a, b |
| Cake | 8/20/2006 | 1441 | 2.86 | 7 | a |
| Winter | 8/21/2006 | 1293 | 2.55 | 0 | a, b |
| Pig | 8/22/2006 | 1650 | 3.30 | 9 | a |
| **2007** | | | | | |
| Rock | 9/5/2007 | - | - | 0 | Trip Blank, a, b |
| Sink | 9/5/2007 | 2086 | 3.96 | 26 | a |

**Table A7: Pesticide Concentration in the Air at Frazee Site B, August 29–September 5, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Bag | 8/29/2007 | - | - | 0 | Trip Blank, a, b |
| Save | 8/29/2007 | 1300 | 2.54 | 9 | a |
| Back | 8/30/2007 | 1541 | 3.16 | 26 | a |
| Sit | 9/4/2007 | 1091 | 2.07 | 59 | a |

**Table A8: Pesticide Concentration in the Air at Frazee Site C, August 22–27, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Nix | 8/22/2007 | - | - | 0 | Trip Blank, a, b |
| Sap | 8/22/2007 | - | - | 0 | Pump Stopped, a, b |
| Ham | 8/24/2007 | 1426 | 2.84 | 24 | a |
| Term | 8/25/2007 | 1445 | 2.89 | 38 | a |
| Big | 8/26/2007 | 1366 | 2.70 | 38 | a |

**Table A9: Pesticide Concentration in the Air at Frazee Site D, June 26–July 29, 2008**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | 2,4-D Concentration ($ng/m^3$) | EBDC Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|---|
| Log | 6/26/2008 | - | - | Not Tested | Not Tested | 0 | Trip Blank, a, k |
| Fix | 6/26/2008 | 1028 | 2.03 | Not Tested | Not Tested | 0 | a, k |
| Pink | 7/7/2008 | 1470 | 2.87 | Not Tested | Not Tested | 0 | a, k |
| His | 7/16/2008 | 1436 | 2.84 | 20 | 7 | Not Tested | m |
| Dust | 7/17/2008 | - | - | 0 | 0 | Not Tested | Trip Blank, c, l |
| Cut | 7/17/2008 | 1454 | 2.84 | 7 | 7 | Not Tested | d, m |
| Fell | 7/18/2008 | 1403 | 2.77 | 7 | 7 | Not Tested | d, m |
| Mud | 7/19/2008 | 1554 | 3.11 | 13 | 115 | Not Tested | |
| Fill | 7/20/2008 | 1284 | 2.57 | 7 | 8 | Not Tested | d, m |
| Well | 7/21/2008 | 1449 | 2.95 | 6 | 7 | Not Tested | d, m |
| Duck | 7/22/2008 | 1440 | 2.88 | 7 | 7 | Not Tested | MV, d, m |
| Must | 7/23/2008 | 1453 | 2.91 | 7 | 7 | Not Tested | d, m |
| Hunt | 7/24/2008 | 1429 | 2.84 | 7 | 7 | Not Tested | d, m |
| Rub | 7/25/2008 | 1407 | 2.79 | 0 | 7 | Not Tested | c, m |
| Luck | 7/26/2008 | 1515 | 3.03 | 6 | 7 | Not Tested | d, m |
| Jump | 7/27/2008 | 1464 | 2.93 | 40 | 7 | Not Tested | m |
| Cup | 7/28/2008 | 1971 | 3.89 | 16 | 18 | Not Tested | |

**Table A10: Pesticide Concentration in the Air at Frazee Site E, June 27–July 28, 2008**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | 2,4-D Concentration ($ng/m^3$) | EBDC Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|---|
| Kick | 6/27/2008 | 1366 | 2.70 | Not Tested | Not Tested | 0 | a, k |
| Him | 6/28/2008 | 504 | 1.01 | Not Tested | Not Tested | 0 | a, k |
| Job | 6/29/2008 | 1300 | 2.54 | Not Tested | Not Tested | 0 | a, k |
| Lock | 7/2/2008 | 1372 | 2.68 | Not Tested | Not Tested | 0 | a, k |
| Fry | 7/2/2008 | - | | Not Tested | Not Tested | 0 | Trip Blank, a, k |
| Lid | 7/6/2008 | 1054 | 2.11 | Not Tested | Not Tested | 0 | a, k |
| Bed | 7/17/2008 | 1444 | 3.01 | 62 | 0 | Not Tested | l |
| Sick | 7/18/2008 | - | | 0 | 0 | Not Tested | Trip Blank, c, l |
| Tub | 7/18/2008 | 1398 | 2.73 | 0 | 0 | Not Tested | c, l |
| Men | 7/19/2008 | 1556 | 3.15 | 0 | 56 | Not Tested | c |
| Top | 7/20/2008 | 1287 | 2.62 | 0 | 27 | Not Tested | c |
| Pot | 7/21/2008 | 1447 | 2.89 | 0 | 20 | Not Tested | c |
| Fun | 7/22/2008 | 1435 | 2.87 | 0 | 0 | Not Tested | c, l |
| Hug | 7/23/2008 | 1452 | 2.87 | 0 | 0 | Not Tested | c, l |
| Cub | 7/24/2008 | 1431 | 2.82 | 5 | 0 | Not Tested | d, l |
| Ten | 7/25/2008 | 1410 | 2.81 | 317 | 0 | Not Tested | l |
| Tell | 7/26/2008 | 1515 | 3.07 | 123 | 0 | Not Tested | l |
| Bump | 7/27/2008 | 1463 | 2.93 | 63 | 0 | Not Tested | l |

**Table A11: Pesticide Concentration in the Air at Frazee Site F, July 17–August 16, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Vest | 7/17/2007 | - | - | 0 | Trip Blank, a, b |
| Sat | 7/17/2007 | 1407 | 2.78 | 8 | a |
| Last | 7/24/2007 | 1471 | 3.94 | 170 | a |
| Talk | 7/25/2007 | 1430 | 2.86 | 158 | a |
| Wag | 7/26/2007 | 1398 | 2.80 | 17 | a |
| Fast | 7/27/2007 | 1489 | 3.02 | 8 | a |
| Ran | 7/28/2007 | 1377 | 2.75 | 15 | a |
| Work | 7/29/2007 | 1641 | 3.28 | 51 | a |
| Bat | 7/30/2007 | 1220 | 2.41 | 120 | a |
| Lap | 7/31/2007 | - | - | 0 | Trip Blank, a, b |
| Lip | 7/31/2007 | 1448 | 2.75 | 190 | a |
| Six | 8/1/2007 | 1489 | 3.02 | 34 | a |
| Cab | 8/4/2007 | 2826 | 5.30 | 23 | a |
| Body | 8/6/2007 | 1395 | 2.89 | 39 | a |
| Jade | 8/6/2007 | - | - | 0 | Trip Blank, a, b |
| Tab | 8/7/2007 | 1524 | 3.09 | 48 | a |
| Pack | 8/8/2007 | 1329 | 2.66 | 65 | a |
| Mine | 8/9/2007 | 1457 | 2.91 | 30 | a |
| Opt | 8/10/2007 | 1441 | 2.95 | 98 | a |
| Saw | 8/11/2007 | 1410 | 2.82 | 11 | a |
| Nose | 8/12/2007 | 1502 | 3.00 | 17 | a |
| Nerd | 8/13/2007 | 1434 | 2.90 | 35 | a |
| Vase | 8/14/2007 | 1362 | 2.72 | 15 | a |
| Win | 8/15/2007 | 1516 | 3.03 | 12 | a |

**Table A12: Pesticide Concentration in the Air at Perham Site A, June 27–July 28, 2008**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | 2,4-D Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|
| Off | 8/1/2008 | 1437 | 2.84 | 23 | 7 | m |
| Tent | 8/2/2008 | - | - | 0 | 0 | Trip Blank, c, l |
| Ripe | 8/2/2008 | 1383 | 2.77 | 7 | 7 | MV, d, m |
| Dime | 8/3/2008 | 1477 | 2.95 | 6 | 7 | d, m |
| Leg | 8/4/2008 | 1437 | 2.87 | 7 | 7 | d, m |
| Made | 8/5/2008 | 1424 | 2.78 | 7 | 7 | d, m |

**Table A13: Pesticide Concentration in the Air at Perham Site B, June 1–August 10, 2008.**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | EBDC Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|
| Seed | 7/1/2008 | - | - | Not Tested | 0 | Trip Blank, a, k |
| Did | 7/1/2008 | 1471 | 2.94 | Not Tested | 0 | a, k |
| Rob | 7/2/2008 | 1419 | 2.80 | Not Tested | 0 | a, k |
| Pick | 7/7/2008 | 1470 | 2.90 | Not Tested | 0 | a, k |
| Will | 7/16/2008 | 1393 | 2.79 | 5 | Not Tested | d |
| Lift | 7/17/2008 | - | - | 0 | Not Tested | Trip Blank, c |
| Hate | 7/31/2008 | 1296 | 2.57 | 6 | Not Tested | d |
| Ask | 8/1/2008 | - | - | 0 | Not Tested | Trip Blank, c |
| End | 8/1/2008 | 1450 | 2.90 | 5 | Not Tested | d |
| Hope | 8/2/2008 | 1391 | 2.75 | 58 | Not Tested | |
| Away | 8/3/2008 | 1479 | 2.96 | 40 | Not Tested | |
| Left | 8/4/2008 | 1431 | 2.86 | 5 | Not Tested | d |
| Best | 8/5/2008 | 1427 | 2.85 | 0 | Not Tested | c |
| Rest | 8/6/2008 | 1460 | 2.96 | 5 | Not Tested | d |
| Yes | 8/7/2008 | 1418 | 2.84 | 164 | Not Tested | |
| Help | 8/8/2008 | 1457 | 2.88 | 74 | Not Tested | |
| Mean | 8/9/2008 | 1737 | 3.47 | 83 | Not Tested | |

**Table A14: Pesticide Concentration in the Air at Perham Site C, July 18–August 14, 2009.**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Chlorpyrifos Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|
| Web | 7/18/2009 | - | - | 0 | 0 | Trip Blank, c, e |
| Day | 7/18/2009 | 1322 | 2.64 | 4 | 0 | d, e |
| Love | 7/19/2009 | 1447 | 2.89 | 4 | 0 | d, e |
| Seen | 7/20/2009 | 1402 | 2.87 | 8 | 0 | e |
| Nest | 7/21/2009 | 1462 | 2.85 | 14 | 0 | e |
| Lost | 7/22/2009 | 1416 | 2.90 | 13 | 0 | e |
| Near | 7/23/2009 | 1493 | 2.99 | 19 | 0 | e |
| Four | 7/24/2009 | 1482 | 2.93 | 10 | 0 | e |
| Born | 7/25/2009 | 1332 | 2.70 | 10 | 0 | e |
| Look | 7/26/2009 | 1478 | 2.96 | 11 | 0 | e |
| Bark | 7/27/2009 | 1476 | 2.95 | 4 | 0 | d, e |
| Town | 7/28/2009 | 1405 | 2.81 | 4 | 0 | d, e |
| Wait | 7/29/2009 | 1423 | 2.85 | 17 | 0 | e |
| Turn | 7/30/2009 | 1421 | 2.84 | 4 | 0 | d, e |
| Mail | 7/31/2009 | 1546 | 3.09 | 8 | 0 | e |
| Park | 8/1/2009 | 1415 | 2.79 | 4 | 0 | d, e |
| Farm | 8/2/2009 | 1466 | 3.01 | 0 | 0 | c, e |
| Sold | 8/3/2009 | 1467 | 3.01 | 11 | 0 | e |
| Yard | 8/4/2009 | 1451 | 2.90 | 4 | 0 | d, e |
| Hard | 8/5/2009 | 1395 | 2.79 | 15 | 0 | e |
| Stay | 8/6/2009 | - | - | 0 | 0 | Trip Blank, c, e |
| Year | 8/6/2009 | 1491 | 2.94 | 16 | 0 | e |
| Rear | 8/7/2009 | 1416 | 2.87 | 4 | 0 | d, e |
| Open | 8/8/2009 | 1405 | 2.81 | 4 | 0 | d, e |
| Fear | 8/9/2009 | 1414 | 2.83 | 13 | 0 | e |
| Weak | 8/10/2009 | 1480 | 2.96 | 4 | 3 | d, f |
| Boat | 8/11/2009 | 1400 | 2.80 | 14 | 6 | |
| Seat | 8/12/2009 | 1467 | 2.93 | 12 | 47 | |
| Corn | 8/13/2009 | - | - | 0 | 0 | Trip Blank, c, e |

**Table A15: Pesticide Concentration in the Air at Pine Point May 15–July 31, 2007**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Pendimethalin Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|---|
| **Site A** | | | | | | |
| Pepper | 5/15/07 | 1437 | 2.95 | 0 | 0 | c,o |
| Pencil | 5/16/07 | 1403 | 2.56 | 0 | 0 | c,o |
| Shoe | 5/17/07 | 1429 | 3.07 | 0 | 0 | c,o |
| Purple | 5/18/07 | 4586 | 8.72 | 0 | 1 | 3-day sample, c |
| Roof | 5/22/07 | 1469 | 2.68 | 0 | 0 | c,o |
| Good | 5/23/07 | 2813 | 5.34 | 0 | 0 | 2-day sample, c,o |
| Apple | 5/25/07 | 5782 | 10.6 | 0 | 0 | 4-day sample, c,o |
| Laurel | 5/29/07 | 8628 | 14.2 | 0 | 0 | 5-day sample, c,o |
| Rain | 6/4/07 | 2865 | 5.66 | 0 | 0 | c,o |
| Boy | 6/6/07 | 5764 | 11.1 | 1 | 11 | 4-day sample |
| Knife | 6/10/07 | 4426 | 7.86 | 1 | 6 | MV, 3-day sample |
| Alpha | 6/13/07 | 7033 | 13.2 | 2 | 6 | MV, 4-day sample |
| Blue | 6/18/07 | 3014 | 6.03 | 0 | 1 | 2-day sample, c |
| Banana | 6/20/07 | 2729 | 5.46 | 0 | 0 | c,o |
| Them | 6/22/07 | 18748 | 35.6 | 1 | 1 | 13-day sample |
| Tire | 7/7/07 | 35967 | 71.9 | 0 | 0 | 24-day sample, c,o |
| Pony | 7/9/07 | 2804 | 5.61 | 4 | 0 | 4-day sample, d |
| Razor | 7/11/07 | 7190 | 14.4 | 1 | 3 | p |
| Marmot | 7/16/07 | 4285 | 8.36 | 2 | 3 | 2-day sample, p |
| Fan | 7/19/07 | 1423 | 2.85 | 4 | 0 | d,o |
| Badger | 7/20/07 | 4305 | 8.39 | 2 | 1 | 2-day sample |
| Play | 7/25/07 | 2887 | 5.49 | 3 | 2 | 2-day sample |
| Pillow | 7/31/07 | 1476 | 2.88 | 3 | 0 | o |
| **Site B** | | | | | | |
| Dog | 5/15/07 | 1406 | 2.72 | 0 | 0 | c,o |
| Shirt | 5/16/07 | 1410 | 2.78 | 0 | 0 | c,o |
| Ogre | 5/17/07 | 5925 | 10.7 | 0 | 1 | MV, 4-day sample, c |
| Lady | 5/21/07 | 2660 | 4.99 | 0 | 3 | MV, c |
| Salt | 5/23/07 | 2811 | 5.41 | 0 | 0 | c,o |
| Bread | 5/25/07 | 5785 | 11.1 | 0 | 1 | 4-day sample, c |
| Joker | 5/29/07 | 4266 | 8.53 | 0 | 1 | 2-day sample, c |
| Sky | 6/1/07 | 4370 | 8.85 | 0 | 1 | 3-day sample, c |
| Mom | 6/4/07 | 2856 | 5.49 | 1 | 0 | o |
| House | 6/6/07 | 5870 | 11.4 | 2 | 1 | 4-day sample |
| Us | 6/11/07 | 2996 | 5.24 | 1 | 0 | MV, 2-day sample, o |
| Omega | 6/13/07 | 7041 | 13.7 | 4 | 4 | 4-day sample, p |
| Bird | 6/18/07 | 2960 | 5.77 | 0 | 0 | 2-day sample, c,o |
| Red | 6/20/07 | 2818 | 3.91 | 11 | 0 | o |
| Fork | 6/22/07 | 18666 | 24.6 | 9 | 0 | 12-day sample, o |
| Pine | 7/5/07 | 5805 | 7.46 | 5 | 0 | 4-day sample, o |
| Snow | 7/9/07 | 2808 | 3.90 | 9 | 0 | o |
| Dad | 7/11/07 | 7199 | 10.0 | 5 | 0 | 5-day sample, o |
| Egg | 7/16/07 | 4276 | 5.79 | 5 | 0 | 2-day sample, o |
| Early | 7/19/07 | 1423 | 2.08 | 27 | 0 | o |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ant | 7/20/07 | 4309 | 5.98 | 0 | 0 | 2-day sample, c,o |
| Wave | 7/31/07 | 1397 | 1.94 | 2 | 0 | o |

**Table A16: Pesticide Concentration in the Air at Staples Site A, June 27–July 12, 2006**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Crab | 6/27/2006 | - | - | 0 | Trip Blank, a, b, n |
| Fish | 6/27/2006 | 1124 | 2.25 | 0 | a, b, n |
| Marmot | 6/28/2006 | 2037 | 3.97 | 45 | a, n |
| Coat | 6/29/2006 | 1611 | 3.22 | 19 | a, n |
| Pine | 6/30/2006 | 754 | 1.51 | 106 | a, n |
| Tire | 7/1/2006 | 1446 | 2.82 | 103 | a, n |
| Star | 7/2/2006 | 1396 | 2.72 | 59 | a, n |
| Purple | 7/3/2006 | 1551 | 3.10 | 35 | a, n |
| Play | 7/4/2006 | 1312 | 2.62 | 30 | a, n |
| Cold | 7/5/2006 | - | - | 0 | Trip Blank, a, b, n |
| Warm | 7/5/2006 | 1516 | 3.03 | 96 | a, n |
| Sand | 7/6/2006 | 1400 | 2.80 | 104 | a, n |
| Ogre | 7/7/2006 | 1611 | 3.14 | 197 | a, n |
| Hot | 7/8/2006 | 4463 | 8.93 | 4 | 3-day sample, a, n |
| King | 7/11/2006 | 1348 | 2.70 | 41 | a, n |

**Table A17: Pesticide Concentration in the Air at Staples Site B, June 18–June 22, 2006**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Roof | 6/18/2006 | - | - | - | Trip Blank, c |
| Pencil | 6/18/2006 | 1713 | 1713 | 0 | c |
| Shoe | 6/19/2006 | 1138 | 1138 | 0 | c |
| Tree | 6/20/2006 | 832 | 832 | 0 | c |
| House | 6/21/2006 | 5436 | 5436 | 0 | 4-day sample, c |

**Table A18: Pesticide Concentration in the Air at Waubun June 25–July 11, 2006**

| Sample Name | Start Date | Total Sample Time (min.) | Total Sample Volume ($m^3$) | Chlorothalonil Concentration ($ng/m^3$) | Notes |
|---|---|---|---|---|---|
| Boy | 6/25/2006 | 3012 | 6.40 | 0 | 2-day sample, c |
| Nail | 6/27/2006 | - | - | 0 | Trip Blank, c |
| Paper | 6/27/2006 | 1242 | 2.64 | 0 | c |
| String | 6/28/2006 | 1404 | 3.05 | 0 | c |
| Grape | 6/29/2006 | 1362 | 3.00 | 0 | c |
| Egg | 6/30/2006 | 1580 | 3.40 | 0 | c |
| Sun | 7/1/2006 | 1414 | 3.11 | 0 | c |
| Robin | 7/2/2006 | 1351 | 2.94 | 0 | c |
| Fox | 7/3/2006 | 1462 | 3.18 | 0 | c |
| Man | 7/4/2006 | 1542 | 3.35 | 0 | c |
| Child | 7/5/2006 | 1284 | 2.76 | 0 | c |
| Wing | 7/6/2006 | 1446 | 3.15 | 0 | c |
| Woman | 7/7/2006 | 1407 | 3.06 | 0 | c |
| Beak | 7/8/2006 | 1410 | 3.03 | 0 | c |
| Glass | 7/9/2006 | 1486 | 3.27 | 0 | c |
| Worm | 7/10/2006 | 1345 | 2.93 | 0 | c |

## Appendix 2: Meteorological Data

Meteorological data were obtained through searching the South Dakota State University archive climate and weather database. Hourly data reported by airport stations near the Drift Catcher sites were used to determine wind direction estimates. This information was analyzed alongside weather data from the precise location of the drift catcher, which was recorded on the Sample Log Sheet. Observations were made for each sampling period at each site, but not all sites are described here.

### Browerville

Weather station data for the area during the monitoring period of July and August 2007 and July 2008 indicate a trend of low wind speeds (0–3mph) from the north and northwest in the morning through mid-day, with an afternoon breeze at an average of 3 mph, and early evening gusts at around 11-12mph. On 8/7/06, wind speeds increased to 8-14 mph from the south and east directions and remained elevated until 8/14/06. At this time, the wind switched direction, coming at the same speed but from the north and northwest. This correlated particularly well with the chlorpyrifos data at Browerville Site B, which shows concentrations exceeding the LOQ from 8/7/06–8/11/06, and then again from 8/13/06–8/14/06, and then dropping below the MDL following the change in wind direction. The strong (9–17mph) southerly and southeasterly winds returned from 8/30–8/31, again correlating with chlorpyrifos concentrations that exceeded the LOQ.

Wind blowing from a neighboring potato field in the direction of the Drift Catcher does not offer a complete explanation for pesticide presence in the air. At Browerville Site C from 8/25/06–8/29/06, air samples were found to contain pesticide concentrations greater than the LOQ, yet wind speeds were from the north or northeast at only 0–5 mph. This implies that pesticide presence in the air could be dependent factors other than a point source in the immediate vicinity, such as a field located father away, or pesticides that have re-volatilized from locations receiving drift on days when the wind was blowing from a source to the site.

### Frazee

The Frazee sites, where sampling took place for the full summer months of 2006, July through September 2007, and June through July 2008, tend to have higher wind speeds of 9–15 mph. In general, morning winds are lower velocity and from the north or northwest, and afternoon and evening winds are 2–10 mph faster and are southerly or southwesterly. However, there was no noticeable pattern for wind direction other than that it most often remained in the same direction for several hours or even days at a time, as opposed to rapidly changing direction and speed.

### Perham

In general, prevailing winds in the summer months of 2008 and 2009 were generally 3–7 mph from the southeast, with some higher speed winds (14–20 mph) from the north. However, occasionally in 2008, southerly winds gust between 22–28mph, as the highest wind speeds tend to have the least predictable direction. The lowest wind speeds tend to be overnight and in the early morning, building throughout the day and peaking in early evening. From 8/02/08–8/09/08, when detectable amounts of chlorothalonil were consistently found in air samples, winds were coming both from the north at 0–5mph and later from the south at 7–14mph. At the Perham Site C location, there was a pattern of low wind speeds overnight and much higher wind speeds throughout the day. Between 12pm–7pm, winds picked up to about 12–20mph, but had a much less predictable direction.

## Appendix 3: Interpreting Air Monitoring Results

Interpreting air monitoring results requires understanding of how U.S. EPA assesses the toxicity of pesticides. In this section we answer the following questions.

*How are "safe" levels of pesticides in air fetermined?*
*Is a chemical more toxic when it is inhaled?*
*Is the REL an air quality standard?*
*Are levels below the REL "safe"?*
*How do PAN's RELs compare to other levels of concern?*
*What do air monitoring results tell us about exposure?*

### How are "safe" levels of pesticides in air determined?

It is generally assumed that humans can be exposed to tiny amounts of most chemicals without suffering ill effects. As doses increase, usually both the severity and incidence of adverse effects increase, hence the adage: "the dose makes the poison." (In recent years, this assumption has been challenged for a class of toxicants known as endocrine disruptors;[43] nonetheless, this idea forms the basis of modern risk assessment.) Thus, rather than trying to prevent any and all exposures to chemicals of concern, regulatory authorities instead try to limit exposure to levels that are so small that the risk of harm is acceptably small.

Risk assessors use a variety of related techniques to quantify the risk posed by exposure to chemicals. These techniques typically involve identifying the highest dose that does not cause observable harm to animals in controlled experiments (the "No Observed Adverse Effect Level," or NOAEL), and then extrapolating from this dose to an acceptable dose in humans that is anticipated to be without harm. This extrapolation accounts for physiological differences between the test animal and humans such as body weight, breathing rate, absorption, and metabolism.

Because the NOAEL is the result of an experiment that uses only several dozen animals (usually rats, mice, or rabbits) that are nearly genetically identical, the extrapolation also includes factors to account for the inherent uncertainty that arises when extrapolating to a human dose that is supposed to be without risk for all members of an exceedingly large and diverse population. An interspecies factor of 10 is generally used to account for the fact that laboratory animals and humans are different and an intraspecies factor of 10 is used to account for variability among different humans. The acceptable human dose calculated with these uncertainty factors is thus typically several orders of magnitude smaller than animal NOAEL that it is based on.

In assessing the risk of dietary exposure to pesticides, U.S. EPA uses oral dosing studies to establish a "Reference Dose" (RfD) following the procedure described above. The Agency defines a RfD as:

> An estimate, with uncertainty spanning perhaps an order of magnitude, of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects of a lifetime.[44]

An RfD should not, therefore, be considered as a threshold level above which adverse effects are guaranteed or even expected. Rather, it should be understood as a level of concern, above which the risk of adverse effects may be unacceptably high (although perhaps still quite small in absolute terms), and below which, the risk is acceptably small. U.S. EPA uses RfDs to set worker protection rules, mitigations for exposures the general public might experience, and acceptable limits for the maximum amount of pesticide residue permissible in food items. With these regulations, the Agency tries to limit human exposure to an amount less than the RfD.

Reference doses are defined specifically for dietary exposure, but similar levels of concern can be derived for inhalation exposure using analogous methods: usually starting with a NOAEL from an animal study and then applying uncertainty factors to extrapolate to an acceptable human dose. The conversion of an acceptable dose (in units of mg of chemical per kg bodyweight per day) to a level of concern (in units of mg or ng of chemical per a certain volume of air) is complicated by variations in breathing rates between laboratory animals and humans, and between different humans. For example, infants and children have proportionately higher breathing rates than adults, so if an infant and an adult are exposed to the same airborne concentration of a toxicant for the same period of time, the infant will receive a larger dose (measured in mg of pesticide per kg of body weight) than the adult. Similarly, breathing rates vary with physical activity, so, for example, a person exercising in contaminated air would receive a higher dose than a person napping in the same environment for the same length of time.

In this air monitoring study, we compare concentrations of pesticides measured in air to 24-hour Reference Exposure Levels (RELs) calculated for a sensitive subpopulation: one-year-old infants. An REL represents a level of concern for inhalation exposure analogous to the Reference Dose that U.S. EPA uses to assess dietary exposure. A REL is an air concentration in nanograms of pesticide per cubic meter of air ($ng/m^3$) equivalent to a dose in milligrams of pesticide per kilogram of body weight (mg/kg) below which the risk of adverse effects is anticipated to be negligible, assuming exposure to a *single pesticide*.[45] These RELs are calculated by PAN starting from the same NOAELs that U.S. EPA uses in its calculations for assessing the inhalation exposure of workers and adjusted for the breathing rate and body weight of an infant. See the **Calculations** section of the report for details.

The methodology we employ is identical to that used by CA DPR to derive screening levels, with exception that we also include the FQPA safety factor used by U.S. EPA in RfD calculations. The California Department of Pesticide Regulation defines a screening level as:

> The calculated air concentration based on a chemical's toxicity that is used to evaluate the possible health effects of exposure to the chemical. Although not a regulatory standard, screening levels can be used in the process of evaluating … air monitoring results. A measured air level that is below the screening level for a given pesticide would not generally undergo further evaluation, should not automatically be considered "safe" and could undergo further evaluation. By the same token, a measured level that is above the screening level would not necessarily indicate a health concern, but would indicate the need for a further and more refined evaluation. Different screening levels are determined for different exposure periods (i.e., acute, subchronic, and chronic).

Exceedances of the REL are not necessarily anticipated to cause the symptoms of acute poisoning described in this report but do represent a potential health concern—the larger the exceedance, the higher the probability of adverse effects from pesticide exposure. It is unknown what exposure levels would produce the chronic effects observed in animal studies for the pesticides found in this study.

#### Is a chemical more toxic when it is inhaled?

The toxicity of chemicals can vary greatly depending on exposure route. For example, U.S. EPA classifies chlorothalonil in its lowest toxicity category (IV) for oral exposure, but in its second highest category (II) for inhalation exposure. Differences in toxicity between oral and inhalation exposure are common, and can arise from differences in absorption between the gastrointestinal and respiratory tracts and from differences in metabolism. Chemicals absorbed from the small intestine are subject to first-pass metabolism by the liver, whereas chemicals entering the body through the lungs are transported immediately into the bloodstream. For this reason, whenever possible, inhalation levels of concern should be based on NOAELs derived from animal inhalation studies. Unfortunately, such studies are

relatively rare, and regulatory agencies often rely on oral studies to assess inhalation risk, a method that may not fully characterize the risks from inhalation exposure.

### Is the REL an air quality standard?

No. The REL is not an enforceable standard like a water quality standard or a worker protection standard. It is analogous to a RfD—a dose that U.S. EPA uses in its dietary assessments as a Level of Concern (LOC). To minimize exposure risk, U.S. EPA typically takes action to reduce dietary exposures of the 99.9$^{th}$ percentile person to below the LOC. This means that if even one-tenth of one percent of the people were exposed to a pesticide in their diet at this level, U.S. EPA would take action to reduce risk. Unfortunately, there are regulatory gaps for inhalation exposure—U.S. EPA has only recently begun to assess bystander inhalation exposures for most pesticides, and in the past assumed that inhalation is not a significant contributor to total exposure. The PAN Drift Catcher work and the work of the California Air Resources Board and the California Department of Pesticide Regulation indicate that this assumption is incorrect. With the release of the draft risk assessment for chlorpyrifos in August 2011, U.S. EPA has started to evaluate inhalation risks from volatilized pesticides. U.S. EPA is scheduled to begin an update of the chlorothalonil risk assessment through the Registration Review process in 2012.

### Are levels below the REL "safe"?

Concentrations below the REL do not necessarily indicate that the air is "safe" to breathe. In particular, a number of recent studies evaluating the people's capacity to metabolize toxic substances show that the variability among different people can be substantially greater than the variability assumed by U.S. EPA in its toxicological analysis.[46] Additionally, people are often exposed to multiple pesticides simultaneously, are taking prescription or non-prescription drugs, or are exposed to other chemicals, thus reducing their capacity to detoxify the pesticides to which they are exposed. Finally, the U.S. EPA's definition of an "adverse" effect does not include symptoms like headache, nausea, or malaise because these are not "observable" symptoms in laboratory animals. These effects are nevertheless uncomfortable and often debilitating for humans, interfering with people's ability to earn a living, perform well in school, take care of their children, or simply be comfortable in their homes.

### How do PAN's RELs compare to other levels of concern?

As noted above, the RELs used in this study are of PAN's own derivation, although they were calculated using U.S. EPA toxicology data and California EPA methodology for deriving RELs.

U.S. EPA has developed Reference Concentrations (RfCs) for some of these pesticides, but these are generally based on NOAELs from oral studies and were calculated using adult breathing rates and body weights. CA DPR has developed screening levels for infants that in some cases are based on inhalation data, but only for a subset of pesticides of interest; in addition, the DPR screening levels do not include the FQPA safety factor for infants and children.

### What do air monitoring results tell us about exposure?

Air monitoring data provide exposure estimates that may or may not represent worst-case exposure scenarios, and do not necessarily represent the precise exposure individuals may experience. Variables that affect an individual's exposure to airborne pesticides include the amount of time spent in areas with high concentrations of airborne pesticides, body weight, and breathing rate. Exposures to the pesticides may also occur through other routes, especially for children. Pesticide drift can contaminate house dust, lawns, playground equipment, pets, and toys that children may touch, and eventually they may ingest these residues.

The breathing rates used to derive the RELs in this study (see the **Calculations** section) represent the breathing rates of individuals *averaged over the course of 24 hours*. An individual child's breathing rate will vary substantially over the course of 24 hours. For example, the typical breathing rate of a 10-year child during resting activity (e.g. sleeping, reading, or watching television) is 0.4 $m^3$/hr, while during

moderate activity (e.g. climbing stairs) it is 2.0 $m^3$/hr, and during heavy activity (e.g. playing sports) is almost ten times greater at 3.9 $m^3$/hr.[47] The breathing rate of a child at play during recess or exercising during a gym class is best approximated by the moderate or heavy activity breathing rate. Thus, children are outside and maximally exposed to air contaminants precisely when their breathing rates are expected to be highest. The RELs used in this report are calculated using lower than moderate breathing rates (the daily averages) and assuming 24-hour exposure. Even though a child is at school for less than 24 hours, during the time she spends there—particularly the time spent playing outside—her breathing rate is higher than the daily average, and thus she may still inhale enough pesticide to exceed the reference dose.

For most pesticides, only a limited number of monitoring studies are available for comparison, and most of the available studies only provide results for applications conducted according to label instructions and for exposure estimates to a single pesticide. The Drift Catcher project is providing additional monitoring data for comparison. As we gather more data, a clearer picture of pesticide levels in air near homes, schools, parks, and workplaces will emerge.

Notwithstanding that available monitoring data are not comprehensive, the data indicate that many people are routinely exposed to levels of airborne pesticides that exceed both acute and sub-chronic levels of concern.

## Appendix 4: Pesticide Information

### Chlorothalonil history

Chlorothalonil is a broad-spectrum fungicide used primarily to combat a variety of mildews, blights, rusts, molds, and scab, as well as some mites and insects. It is preventative and non-systemic, and therefore is often applied up to ten times over the course of a growing season.[20]

In the United States, chlorothalonil is primarily manufactured by GB Biosciences and Sipcam Agro USA Inc., and distributed under trade names including Bravo, Daconil, Echo, and Tuffgard. The chemical was first registered in the U.S. in 1966 for use on turf grass by Diamond Shamrock Co., and in 1970 for use on food crops, starting with potatoes.[20]

### Use

In 1997, chlorothalonil was the third most widely used fungicide in the United States, with nearly 12 million pounds applied to food crops each year.[48] In 1999, U.S. EPA estimated that the crops with the highest annual usage of chlorothalonil were peanuts (7 million lbs/yr), potatoes (3.5 million lbs/year), and tomatoes (1.5 million lbs/yr). The crops with the highest percentage of acreage treated annually included celery (79-100%), peanuts (72-93%), onions (62-93%) and cucumbers (59-83%). It is also used heavily for non-agricultural applications: as a fungicide on golf courses (1.5 million lbs/yr) and as a preservative in paint (2 million lbs/yr).[20] Chlorothalonil is no longer used on home lawns and gardens, but continues to be applied to ornamental plants and Christmas trees.[49]

Most chlorothalonil products are sold as a powder, concentrate, or water dispersible granule, that is then mixed with water prior to application. Since chlorothalonil is non-systemic, it is sprayed directly onto the plant foliage by aerial or ground equipment, or through sprinkler irrigation.[49]

In Minnesota, chlorothalonil is used primarily on potatoes, and also for carrots, onions, pumpkins, and dry beans.[50] A total of 634,692 lbs of chlorothalonil were purchased in Minnesota in 2009, 68% of which was sold in the form of a crop chemical. According to data ranging from 2004 to 2009, sales (in lbs) of chlorothalonil have increased annually at an average rate of 11.07%.[51]

### Ecological toxicity

The effect of chlorothalonil on wildlife differs substantially between terrestrial and aquatic species. In general, chlorothalonil has a low bioaccumulation potential, and has been found to have low acute (immediate) toxicity to avian species and small mammals. While U.S. EPA has found chlorothalonil to be "relatively non-toxic" to honey bees, more recent independent studies have detected an accumulation of chlorothalonil in hive pollen that results in a higher risk of hive mortality in the field.[52,53] Chlorothalonil and SDS-3701, its most toxic degradate, pose a much greater threat to marine life. Chlorothalonil is "very highly toxic" to fish and aquatic invertebrates,[52] affecting reproduction at between 3 and 6.5 ppb, and 39 and 79 ppb, respectively.

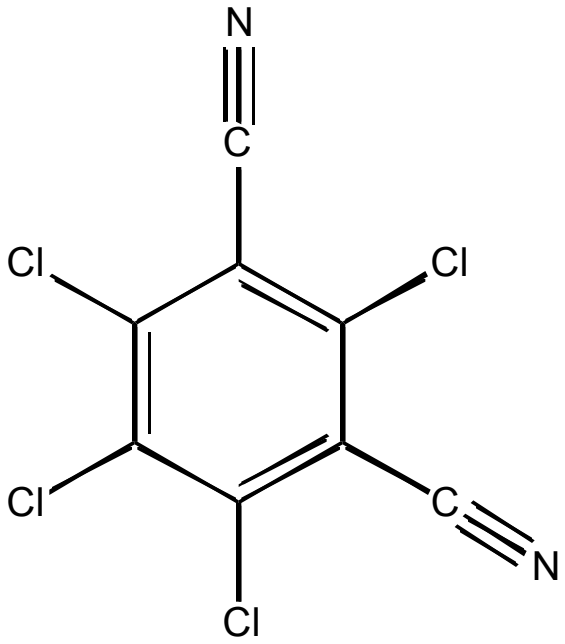
Frogs, which have both terrestrial and aquatic phases, are at high risk of being exposed to chlorothalonil. A study designed in response to the listing of the California Red Legged Frog (CRLF) as an endangered species looked at the potential risk to CRLF as a result of chlorothalonil use. It was found that not only are CRLFs directly affected by the toxins chlorothalonil and SDS-3701, their prey base, and thus their dependent ecosystem, is in jeopardy.[54]

### Physical properties of chlorothalonil

Chlorothalonil [2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile; tetrachloroisophthalonitrile] is an aromatic halogenated compound and a member of the chloronitrile family. Technical chlorothalonil is an odorless white crystalline solid.[55] Thermally and chemically stable in its pure form, it is non-

corrosive and resistant to breakdown under normal UV radiation and in neutral aqueous solutions. In soils, it has an average aerobic half-life of 35 days. With a vapor pressure of $2x10^{-6}$, it is of moderate to low volatility. Chlorothalonil is non-systemic, meaning it does not translocate from the site of application to other parts of the plant.[56] Chlorothalonil is a glutathione inhibitor: it reacts with glutathione molecules inside fungal cells to inhibit glutathione-dependent enzymes. These enzymes are essential for cellular respiration.

The chemical structure of chlorothalonil is shown below.




In the production of chlorothalonil, hexachlorobenzene (HCB) is produced as an impurity. A maximum of 40 ppm is the upper limit for HCB content in chlorothalonil. This impurity is more acutely toxic than chlorothalonil itself and is classified as a B2 "probable" carcinogen. [25]

When chlorothalonil breaks down in soil, 4-hydroxy-2,5,6-trichloroisophthalonitrile is produced. This compound, also known as SDS-3701, is about 30 times more acutely toxic than chlorothalonil and is more persistent in the environment.[56,57]

## Appendix 5: Sample Log Sheet

**Drift Catcher Sample Log Sheet**

### STARTING THE SAMPLE

Project: _____ Location: _____

**YOU NEED**: A Drift Catcher, a sample bag with pre-labeled tubes, caps, and labels, a tube cracker, a rotameter, two light shields, orange flag material, a compass, and a wind meter.

❒ **1. LABELS:** Make sure the labels included in the sample bag MATCH the labels on the pre-labeled tubes. If they match, affix the labels to this log sheet under Steps 4 & 11.

❒ **2. TUBES:** Break the tips of the glass sample tubes and insert them into the manifold.

❒ **3. PUMP:** Plug in the pump and note the EXACT TIME using the clock on the compass.

| Today's Date | | Exact Pump START Time | **AM or PM?** |
|---|---|---|---|

❒ **4. ROTAMETER:** Use the rotameter to measure the flow rate for each tube.

| | Tube Name | Starting Flow Rate | |
|---|---|---|---|
| Tube A | [stick label here] | **L/min** | **NOTE: Adjust the flow rates so that they are equal to each other!** |
| Tube B | [stick label here] | **L/min** | |

❒ **5. LIGHT SHIELDS:** Attach both light shields.

❒ **6. COMPASS & ORANGE FLAG:** Use these to find the direction of the wind.

| Which direction is the wind blowing FROM? | N NE E SE S SW W NW calm |
|---|---|

❒ **7. WIND METER:** Face the wind meter into the wind for 2 minutes.

| What is the wind speed? | maximum: mph | average: mph |
|---|---|---|
| What is the temperature? **(Remember to wave wind meter back and forth!)** | | °F |

❒ **8. YOUR SENSES:** Use your own senses to answer the following questions.

| What is the weather like? | foggy sunny mix of sun and clouds cloudy rainy humid other: |
|---|---|
| Do you smell anything? | sweet rotten eggs perfume skunk none other: |

There is space for other observations and notes at the bottom of the other side of this page.

Name: _____ Initials: _____

## STOPPING THE SAMPLE (cont'd from other side)

❒ **9. PUMP:** Is the pump running? ❒ Yes ❒ No (If not, skip to Step #13)

❒ **10. LIGHT SHIELDS:** Remove both light shields.

❒ **11. ROTAMETER:** Use the rotameter to measure the flow rate for each tube.

| | Tube Name | Ending Flow Rate | |
|---|---|---|---|
| Tube A | [stick label here] | L/min | **DO NOT adjust the flow rates. Just measure them.** |
| Tube B | [stick label here] | L/min | |

❒ **12. PUMP:** Unplug the pump and note the EXACT TIME, using the clock on the compass.

| Today's Date | | Exact Pump STOP Time | **AM or PM?** |
|---|---|---|---|

❒ **13. TUBES:** Remove the sample tubes, cap them, place them in the sample bag.

❒ **14. COMPASS & ORANGE FLAG:** Use these to find the direction of the wind.

| Which direction is the wind blowing FROM? | N NE E SE S SW W NW calm |
|---|---|

❒ **15. WIND METER:** Face the wind meter into the wind for 2 minutes.

| What is the wind speed? | maximum: mph | average: mph |
|---|---|---|
| What is the temperature? **(Remember to wave wind meter back and forth!)** | | °F |

❒ **16. YOUR SENSES:** Use your own senses to answer the following questions.

| What is the weather like? | sunny mix of sun and clouds cloudy rainy humid other: |
|---|---|
| Do you smell anything? | sweet rotten eggs perfume skunk none other: |

❒ **17. TRIP BLANK:** If this is the first sample of your sample run in this location, prepare a Trip Blank sample (follow instructions on Trip Blank form).

Name: _____ Initials: _____

---

### OBSERVATIONS AND NOTES

Please record observations or notes below (known pesticide applications nearby, equipment failure, nearby activities that could interfere with the sample, etc.)

| Date | Time | Observation/Note |
|---|---|---|
| | | |

## Appendix 6: Freezer Log and Chain of Custody Form

### Chain of Custody Form and Freezer Log

This form is used to keep track of where all your samples are and who has been responsible for them at all times.

Name: _____ Phone Number: _____

Project Name: _____

Sample Site (Include full address): _____

_____

Date Sampling Started: _____ Date Sampling Finished: _____

**Freezer Log**

| Sample Name | Sample Placed in Freezer on Date | Time (am/pm) | Notes or Comments | Initials |
|---|---|---|---|---|
| Ejemplo – A | 6/8/05 | 8:18 pm | This is an example entry. | JD |
| | | | | |
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Pesticide Action Network, 49 Powell Street, Suite 500, San Francisco, CA 94102, (415) 981-1771

**Chain of Custody Form**

This section tracks who has control of the batch of samples as they are being transported and how they are handled.

When you receive the samples,
- Make sure all samples are accounted for.
- Record the time and date and put your initials in the **Received by** column.
- If you are unpacking samples from a shipping box, note the temperature of the ice packs.

When samples are passed from one person to another, you should record the method of storage (freezer, cooler, dry ice, etc). If you change the method of storage (i.e. from a freezer to a cooler) please also record this along with the date and time of change, even though the samples are still in your custody.

| Date Sent | Time Sent | Sent by (Initials) | Storage Before Transfer | Storage During Transfer | Storage After Transfer | Date Received | Time Received | Received by (Initials) | Temperature upon arrival (Circle one)* |
|---|---|---|---|---|---|---|---|---|---|
| 6/9/05 | 2:43 pm | JD | Freezer | Cooler | Freezer | 6/10/05 | 9:08 am | SK | (1) - 2 - 3 - 4 |
| | | | | | | | | | 1 - 2 - 3 - 4 |
| | | | | | | | | | 1 - 2 - 3 - 4 |
| | | | | | | | | | 1 - 2 - 3 - 4 |
| | | | | | | | | | 1 - 2 - 3 - 4 |

*note the shipping container temperature by choosing the ice pack description that best describes the condition of the ice packs.
1: Fully frozen; 2: Partially frozen; 3: Not frozen but still cold; 4: Room Temperature

**Names and signatures of sample handlers:**

Each person who handles the samples will need to sign off on this form. Your signature and initials are your verification that the samples were handled as indicated on the form.

| | Name (Please print) | Phone Number | Signature | Initials |
|---|---|---|---|---|
| Example | Juan Diego | (234) 567-8901 | Juan Diego | JD |
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 4 | | | | |

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## Appendix 7: Standard Operating Procedures for Sample Extraction

*QuickView*

- ❑ Label extraction vials for samples and lab blanks
- ❑ Enter extraction date, solvent and volume into DCD database
- ❑ Print sample processing form and put in project notebook
- ❑ Record extraction in lab notebook
- ❑ Prepare lab blanks & lab spikes
- ❑ Crack tubes into vials, add solvent, allow to sit
- ❑ Optional: Sonicate, make sure labels won't fall off
- ❑ Label GC vials, 2 for each resin bed (front/back)
- ❑ Transfer samples to GC vials. Check caps for tightness (dent in cap).
- ❑ Run or store in freezer

1. This method is based on NIOSH Method 5600. Label a set of 6 mL vials (Teflon-lined caps)—two for each sample tube, one for the front resin bed and one for the back resin bed. The labeling convention is as follows: the sample name, tube letter (A or B), and the front or back bed specification. For example, if the tube has a label that says TREE-A, the name on the first sample vial containing the front bed would be labeled TREE-A-F and the back bed vial would be labeled TREE-A-R.

2. Enter the extraction date, solvent and solvent volume into the Drift Catcher Data (DCD) database. Also, record the extraction in the lab notebook.

3. Prepare two lab blanks using sorbent tubes (or filters) with the same lot number(s) as your samples, labeling them with the lot number in the name, e.g. Blank3658-1, Blank3658-2, for two blanks of lot number 3658. Crack the tube open by using a glass file to score the tube near the front glass wool plug, then snapping the tube in two. Using a dental pick, remove the glass wool plug and then pour the front resin bed (the glass wool can be discarded) into an extraction vial and extract according to the directions used for samples below.

4. Prepare the lab spikes using sorbent tubes (or filters) with the same lot number as the samples. Crack a tube open as above, pour the front resin bed (the glass wool is not necessary) into an extraction vial and spike with a known amount of the pesticide or group of pesticides you are likely to find. Spike with an amount that will give a final concentration in that falls within the expected range of the samples. Allow to sit for at least 30 minutes. If there is no knowledge of what pesticide is present, wait to do the spikes until after the pesticide present has been identified.

5. Crack open the sample tubes. Transfer both the first glass wool plug and the front bed of resin (the larger of the two resin beds) into a labeled 6 mL sample vial with a Teflon-lined cap. As you do this step, double-check that the label on the vial matches the label on the tube. Remove the second glass wool plug and back resin bed into another labeled sample vial. Before processing any samples, don't forget to make lab blanks, and spikes if the pesticide has been identified.

6. After the tubes are cracked and the contents placed in vials for samples, blanks and spikes, use a micropipette to pipette 2.00 mL of ethyl acetate into each sample vial. Invert the samples several times and allow them to sit for 30 minutes, shaking the vials occasionally during this time period.

7. OPTIONAL: Place the tubes in the sonicator for 30 minutes (six cycles of five minutes each). Care needs to be taken when placing the samples in the sonicator so the labels don't get wet and fall off. Putting the

labels on the caps is best—they should be moved to the vial after extraction.

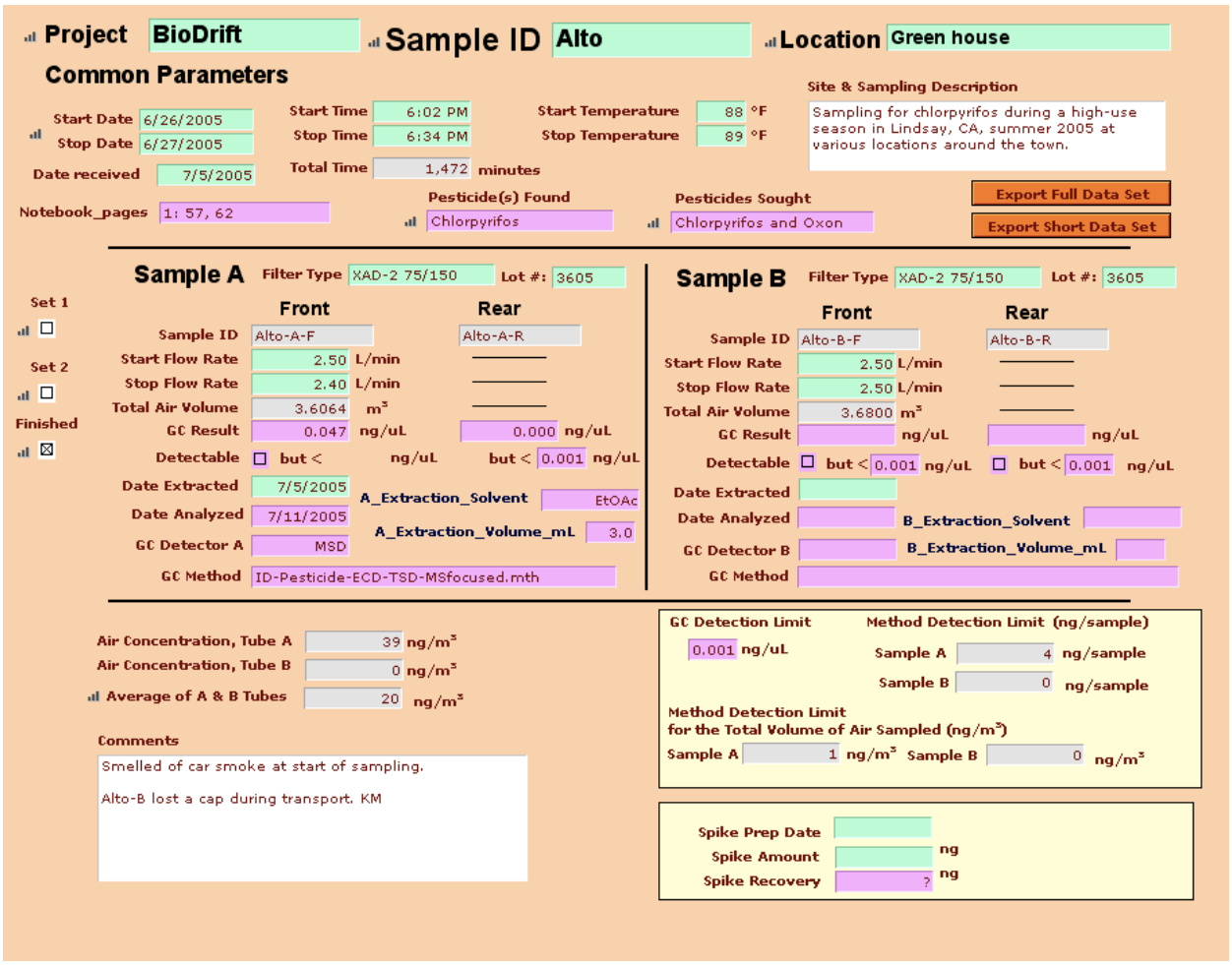
8. **NOTE:** Some pesticide extractions do not require sonication—the extraction seems to work just as well by letting the vials sit for 30 minutes with occasional shaking. The NIOSH method explicitly says not to use sonication, but the U.S. EPA method says that the samples should be sonicated. So far, we haven't found it to make a difference for OP pesticides.

9. After removal from the sonicator, the samples are pipetted as soon as possible (within the next 30 minutes), into GC autosampler vials for analysis (Restek #21141 with caps, Restek #24670). Check the caps to be sure they are sealed tight—they should be obviously indented in the middle.

   **NOTE:** For every 6 mL vial of sample extract, two autosampler vials can be filled. It is recommended that two autosampler vials be filled from each extraction vial so that a backup sample is available if the first GC run fails for any reason or if the first sample needs to be used to ID the pesticide(s) present. At this point, there are FOUR autosampler vials for every resin tube (two from the front bed and two from the back).

10. Store the autosampler vials in the freezer unless the samples are to be run immediately.

## Appendix 8: Sample Log Database Screen Shot



## Appendix 9: Instrument Parameters for Sample Analysis

All samples were analyzed using a Varian 3800 gas chromatograph equipped with two injector ports, a CP-8400 autosampler, electron capture detector (ECD) and Saturn 2200 ion trap mass selective detector (MSD). Samples were quantified using the ECD, with the MSD used to verify the identity of sample components. The column used was a Restek Rxi-5ms capillary GC column, 30 m x 0.25 mm, 0.25 mm film thickness. Split injection was employed using a variety of split ratios to bring the analytes and calibration standards into the linear range of the ECD. The LOQs, IDLs, and MDLs quoted in the body of this text reflect the detection limits of the most sensitive method (lowest split ratio) for each analyte. Prior to analytical runs using the MSD, the MSD was autotuned to set the electron multiplier gain and calibrate mass setpoints on PFTBA ions.

### Table A-5: Gas Chromatograph Parameters

| Injector Temp. | Detector Temp. | GC Column Oven Temperature Program | | | | Flow Rates (mL/min) | |
|---|---|---|---|---|---|---|---|
| | | Temp (°C) | Heating Rate (°C/min) | Hold Time (min) | Total Time (min) | Carrier Gas (He) | Makeup Gas ($N_2$) |
| 250 °C | 300 °C (ECD) | 120 | 0 | 0.5 | 0.5 | 1 | 30 |
| | | 200 | 4 | 0 | 20.5 | | |
| | | 260 | 10 | 9.0 | 35.5 | | |
| | | 300 | 20 | 5.0 | 42.5 | | |

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